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(54) 【発明の名称】 インクジェット用記録材料

(57) 【要約】

【課題】 光沢、白色性、およびインク吸収性が良好で、  
画像の耐候性と発色性に優れたインクジェット用記録材  
料を提供する。

【解決手段】 耐水性支持体上に少なくとも1層のインク  
受容層を有するインクジェット用記録材料において、該  
インク受容層が、無機微粒子、親水性バインダー、およ  
び蛍光増白剤を含有し、更に、ヒドラジン誘導体、含イ  
オウ有機化合物、および糖類の少なくとも1種を含有す  
ることを特徴とするインクジェット用記録材料。特に、

(2)

特開2003-285535

1

## 【特許請求の範囲】

【請求項1】 耐水性支持体上に少なくとも1層の無機微粒子、および親水性バインダーを含有するインク受容層を有するインクジェット用記録材料において、該インクジェット用記録材料が、蛍光増白剤を含有し、更に、ヒドラジン誘導体、含イオウ有機化合物、および糖類の少なくとも1種を含有することを特徴とするインクジェット用記録材料。

【請求項2】 前記インク受容層が2層以上であり、前記支持体に近いインク受容層が蛍光増白剤を含有し、前記支持体から離れたインク受容層がヒドラジン誘導体、含イオウ有機化合物、および糖類の少なくとも1種を含有することを特徴とする請求項1に記載のインクジェット用記録材料。

【請求項3】 耐水性支持体上に少なくとも2層の無機微粒子、および親水性バインダーを含有するインク受容層を有するインクジェット用記録材料において、該支持体に近いインク受容層が蛍光増白剤の少なくとも1種を含有しており、該支持体から離れたインク受容層がカチオン性化合物を含有していることを特徴とするインクジェット用記録材料。

【請求項4】 耐水性支持体上に少なくとも2層の無機微粒子、および親水性バインダーを含有するインク受容層を有するインクジェット用記録材料において、該支持体に近いインク受容層が蛍光増白剤の少なくとも1種を含有しており、該支持体から離れたインク受容層の無機微粒子がアルミナ、およびアルミナ水和物の少なくとも1種であることを特徴とするインクジェット用記録材料。

【請求項5】 前記支持体から離れたインク受容層がヒドラジン誘導体、含イオウ有機化合物、および糖類の少なくとも1種を含有することを特徴とする請求項3または4に記載のインクジェット用記録材料。

【請求項6】 前記ヒドラジン誘導体が、カルボノヒドラジド誘導体およびセミカルバジド誘導体の少なくとも1種である請求項1、2または5に記載のインクジェット用記録材料。

【請求項7】 前記蛍光増白剤がカチオン性有機蛍光増白剤である請求項1～6の何れか1項に記載のインクジェット用記録材料。

2

を特徴とする請求項2～9の何れか1項に記載のインクジェット用記録材料。

【請求項11】 前記支持体から離れたインク受容層が蛍光増白剤を含有していないことを特徴とする請求項2～10の何れか1項に記載のインクジェット用記録材料。

【請求項12】 前記インク受容層がメチロールアミノ系化合物を含有していることを特徴とする請求項1～11の何れか1項に記載のインクジェット用記録材料。

## 【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、高い光沢と白色性を有し、インク吸収性が良好なインクジェット用記録材料に関し、更に詳しくは、耐賞変性、印字画像の発色性、ひび割れ、および耐候性が良好なインクジェット用記録材料に関するものである。

【0002】

【従来の技術】インクジェット記録方式に使用される記録材料として、通常の紙やインクジェット記録用紙と称される支持体上に非晶質シリカ等の顔料をポリビニルアルコール等の水溶性バインダーからなる多孔質のインク受容層を設けてなる記録材料が知られている。

【0003】例えば、特開昭55-51583号、同56-157号、同57-107879号、同57-107880号、同59-230787号、同62-160277号、同62-184879号、同62-183382号、及び同64-11877号公報等に関示のごとく、シリカ等の含珪素顔料を水系バインダーと共に紙支持体に塗布して得られる記録材料が提案されている。

【0004】また、特公平3-56552号、特開平2-188287号、同平10-81064号、同平10-119423号、同平10-175365号、同平10-193776号、同10-203006号、同10-217601号、同平11-20300号、同平11-20306号、同平11-34481号公報等公報には、気相法による合成シリカ微粒子（以降、気相法シリカと称す）を用いることが開示されている。また、特開昭62-174183号、特開平2-276670号、特開平5-32037号、特開平6-199034号公報等にアルミナやアルミナ水和物を用いた記録材料が開

(3)

特開2003-285535

3

加工された紙支持体、例えば、紙の両面にポリエチレン等のポリオレフィン樹脂をラミネートした樹脂ラミネート紙（ポリオレフィン樹脂被覆紙）、プラスチックフィルム等が用いられるようになってきた。しかしながら、耐水性支持体は、紙支持体と違ってインクを吸収することができないため、支持体上に設けられたインク受容層のインク吸収性が重要であり、インク受容層の空隙率を高める必要がある。従って、気相法シリカ等の無機微粒子の塗布量を多くし、更に、無機微粒子に対するバインダーの比率を低減する必要がある。

【0006】しかしながら、インク受容層に気相法シリカ等の無機微粒子を高比率で用い、バインダーの比率を下げた多孔質記録材料は、保管中に白紙部が変色しやすいという問題を有している。即ち、ファイル等での保存時にインク受容層に吸着されたフィルム由来の可塑剤や酸化防止剤が、光、熱、および大気中の微塵ガス等により酸化されることにより黄変（以下、ファイル黄変と記す）する。また、元々インク受容層に含有のバインダー、界面活性剤、媒染剤、顔料等が光、熱、大気中の微塵ガス等で劣化することによる黄変（以下、劣化黄変と記す）する。

【0007】特開平7-68920号公報には、黄変防止のために蛍光増白剤を含有する多孔質インク受容層を有する記録シートが開示されている。しかしながら、蛍光増白剤自身が不安定なために自身の劣化による黄変が発生しやすく、画像の耐光性も低下傾向となった。特開2000-211247号公報には、視感白色性改良のために記録層の少なくとも1層が、着色剤と蛍光染料の少なくとも1種、および平均粒径が1μm以下の顔料を含有し、不透明度が50%以下とした記録体が開示されているが、特定の層構成や添加剤による黄変改良、発色性に関しては記載されていない。特開2001-246833号公報には、保存時の黄変を抑制するために蛍光増白剤含有の多孔質インク受容層を有し、インク受容層側の表面pHを4.5以上6.5以下とする記録媒体が開示されているが劣化黄変に対しては不十分であり、特定の層構成や添加剤による黄変改良、画像の耐候性改良に関しては記載されていない。

【0008】また、微塵ガスによる印字画像の退色防止剤、耐光性改良剤として知られている化合物は、無機微

4

含有させることで耐ガス性を改良する提案がなされているが、層構成や蛍光増白剤との併用による耐黄変改良や画像保存性改良についての記載は無い。特開昭61-154989号公報には、合成シリカからなるインク受容層にヒドラジド化合物を含有させることで耐光性が改良されることが記載されているが、耐ガス性の悪化が懸念され、耐黄変に関する記載も無く、ヒドラジド系化合物を多孔質インク受容層へ使用した場合にインクにより印字画像の経時でのひび割れが発生しやすい傾向があった。

10 特開平7-314881号公報には、多孔質インク受容層に尿素誘導体、セミカルバジド誘導体、カルボヒドラジド誘導体、およびヒドラジン誘導体の少なくとも1種を含有させることで白紙部分の黄変を防止する提案がなされているが、蛍光増白剤との併用、層構成による黄変防止、および画像の耐候性についての記載は無い。

【0010】

【発明が解決しようとする課題】更に、本発明者らは、蛍光増白剤を用いたインク受容層にインクジェットで印字した場合の問題として画像の耐候性低下に加え、発色性が低下しやすいことを見出した。

【0011】従って、本発明の目的は、高い光沢性、白色性を有し、インク吸収性が良好で経時による白紙部の黄変が起りにくく、印字された画像部の耐候性、発色性が良好なインクジェット用記録材料を提供することにある。

【0012】

【課題を解決するための手段】本発明者らは、上記課題について種々検討した結果、主として下記的手段により本発明の目的が達成された。

30 【0013】（1）耐水性支持体上に少なくとも1層のインク受容層を有するインクジェット用記録材料において、該インクジェット用記録材料が、無機微粒子、親水性バインダー、および蛍光増白剤を含有し、更に、ヒドラジン誘導体、含イオウ有機化合物、および糖類の少なくとも1種を含有することを特徴とするインクジェット用記録材料。

【0014】（2）前記インク受容層が2層以上であり、前記支持体に近いインク受容層が蛍光増白剤を含有し、前記支持体から離れたインク受容層がヒドラジン誘導体、含イオウ有機化合物、および糖類の少なくとも1

(4)

特開2003-285535

5

無機微粒子、および親水性バインダーを含有するインク受容層を有するインクジェット用記録材料において、該支持体に近いインク受容層が蛍光増白剤の少なくとも1種を含有しており、該支持体から離れたインク受容層の無機微粒子がアルミナ、およびアルミナ水和物の少なくとも1種であることを特徴とするインクジェット用記録材料。

【0017】(5) 前記蛍光増白剤がカチオン性有機蛍光増白剤である前記(1)～(4)の何れかに記載のインクジェット用記録材料。

【0018】(6) 前記耐水性支持体から離れたインク受容層が蛍光増白剤を含有していないことを特徴とする前記(1)～(5)の何れかに記載のインクジェット用記録材料。

【0019】(7) 前記インク受容層がメチロールアミノ系化合物を含有していることを特徴とする前記(1)～(6)の何れかに記載のインクジェット用記録材料。

【0020】

【発明の実施の形態】以下、本発明を詳細に説明する。本発明に用いられる耐水性支持体としては、ポリエチレンテレフタレート等のポリエステル樹脂、シアセテート樹脂、トリアセテート樹脂、アクリル樹脂、ポリカーボネート樹脂、ポリ塩化ビニル、ポリイミド樹脂、セロハン、セルロイド等のプラスチック樹脂フィルム、および紙の少なくとも片面にポリオレフィン樹脂をラミネートした樹脂被覆紙が挙げられる。本発明に用いられる耐水性支持体の厚みは、約50～300 $\mu$ m程度が好ましい。

【0021】本発明において好ましく用いられる樹脂被覆紙を構成する原紙は、特に制限はなく、一般に用いられている紙が使用できるが、より好ましくは例えば写真用支持体に用いられているような平滑な原紙が好ましい。原紙を構成するパルプとしては天然パルプ、再生パルプ、合成パルプ等を1種もしくは2種以上混合して用いられる。この原紙には一般に製紙で用いられているサイズ剤、紙力増強剤、染料、帯電防止剤、蛍光増白剤、染料等の添加剤が配合される。

【0022】さらに、表面サイズ剤、表面紙力剤、蛍光増白剤、帯電防止剤、染料、アンカー剤等が表面塗布されていてもよい。

6

ポリオレフィン樹脂としては、低密度ポリエチレン、高密度ポリエチレン、ポリプロピレン、ポリブテン、ポリペンテンなどのオレフィンのホモポリマーまたはエチレン-プロピレン共重合体などのオレフィンの2つ以上からなる共重合体及びこれらの混合物であり、各種の密度、熔融粘度指数(メルトインデックス)のものを単独にあるいはそれらを混合して使用できる。

【0025】また、樹脂被覆紙の樹脂中には、酸化チタン、酸化亜鉛、タルク、炭酸カルシウムなどの白色顔料、ステアリン酸アミド、アラキジン酸アミドなどの脂肪酸アミド、ステアリン酸亜鉛、ステアリン酸カルシウム、ステアリン酸アルミニウム、ステアリン酸マグネシウムなどの脂肪酸金属塩、イルガノックス1010、イルガノックス1076などの酸化防止剤、コバルトブルー、群青、セシリアンブルー、フタロシアニンブルーなどのブルーの顔料や染料、コバルトバイオレット、ファストバイオレット、マンガン紫などのマゼンタの顔料や染料、蛍光増白剤、紫外線吸収剤などの各種の添加剤を適宜組み合わせる加えるのが好ましい。

【0026】本発明において好ましく用いられる支持体である樹脂被覆紙は、ポリオレフィン樹脂の場合は、走行する原紙上に加熱溶融した樹脂を流延する、いわゆる押出コーティング法により製造され、そのおもて面または両面が樹脂により被覆される。また、電子線により硬化する樹脂の場合は、グラビアコーター、ブレードコーターなど一般に用いられるコーターにより樹脂を塗布した後、電子線を照射し、樹脂を硬化させて被覆する。また、樹脂を原紙に被覆する前に、原紙にコロナ放電処理、火炎処理などの活性化処理を施すことが好ましい。支持体のインク受容層が塗布される面(おもて面)は、その用途に応じて光沢面、マット面などに加工される。裏面に樹脂を被覆する必要はないが、カール防止の点から樹脂被覆したほうが好ましい。裏面は通常無光沢面であり、表面あるいは必要に応じて表裏両面にもコロナ放電処理、火炎処理などの活性処理を施すことができる。また、樹脂被覆層の厚みとしては特に制限はないが、一般に片面5～50 $\mu$ mの厚みに表面または表裏両面にコーティングされる。特に、樹脂被覆時に樹脂層表面を型付けされたクーリングロールに押圧することや樹脂被覆紙を型付けロールで後加工すること等により樹脂被覆紙

(5)

特開2003-285535

7

【0027】本発明における支持体には帯電防止性、搬送性、カール防止性などのために、各種のバックコート層を塗設することができる。バックコート層には無機帯電防止剤、有機帯電防止剤、親水性バインダー、ラテックス、硬化剤、顔料、界面活性剤などを適宜組み合わせで含有せしめることができる。また、支持体とインク受容層との接着性や親和性を向上させるために支持体に顔料、親水性バインダー、ラテックス、硬化剤等を適宜含有した下塗り層を設けても良い。

【0028】本発明のインク受容層に用いられる無機微粒子としては、平均一次粒径が $1\mu\text{m}$ 以下であり、シリカ、アルミナ、アルミナ水和物、炭酸カルシウム、炭酸マグネシウム等公知の各種微粒子が挙げられるが、特にシリカ、アルミナ水和物が好ましい。インク受容層には、無機微粒子を $8\text{g}/\text{m}^2$ 以上含有するのが好ましく、 $10\sim 40\text{g}/\text{m}^2$ の範囲で用いるのがより好ましい。この範囲より少ないと、インク吸収性が劣る。ポリビニルアルコール量は、無機微粒子に対して40質量%以下、好ましくは35質量%以下であり、特に8～25質量%が好ましい。

【0029】本発明において使用される無機微粒子は、インク吸収層中の主たる割合、すなわち全固形分に対して無機微粒子を50質量%以上、好ましくは60質量%以上、より好ましくは65質量%以上含有することが好ましい。

【0030】合成シリカには、湿式法によるものと気相法によるものがある。湿式法シリカとしては、①ケイ酸ナトリウムの酸などによる複分解やイオン交換樹脂層を通して得られるシリカゾル、または②このシリカゾルを加熱熱成して得られるコロイダルシリカ、③シリカゾルをゲル化させ、その生成条件を変えることによって数ミクロンから10ミクロン位の一次粒子がシロキサン結合をした三次元的な二次粒子となったシリカゲル、更には④シリカゾル、ケイ酸ナトリウム、アルミン酸ナトリウム等を加熱生成させて得られるもののようなケイ酸を主体とする合成ケイ酸化化合物等がある。

【0031】気相法シリカは、湿式法に対して乾式法とも呼ばれ、一般的には火炎加水分解法によって作られる。具体的には四塩化ケイ素を水素及び酸素と共に燃焼して作る方法が一般的に知られているが、四塩化ケイ素

8

ものを用いることである。本発明で云うBET法とは、気相吸着法による粉体の表面積測定法の一つであり、吸着等温線から1gの試料の持つ総表面積、即ち比表面積を求める方法である。通常吸着気体としては、窒素ガスが多く用いられ、吸着量を被吸着気体の圧、または容積の変化から測定する方法が最も多く用いられている。多分子吸着の等温線を表すのに最も著名なものは、Brunauer, Emmett, Tellerの式であってBET式と呼ばれ表面積決定に広く用いられている。BET式に基づいて吸着量を求め、吸着分子1個が表面で占める面積を掛けて、表面積が得られる。

【0033】本発明のアルミナとしては酸化アルミニウムの $\gamma$ 型結晶である $\gamma$ -アルミナが好ましく、中でも $\delta$ グループ結晶が好ましい。 $\gamma$ -アルミナは一次粒子を10nm程度まで小さくすることが可能であるが、通常は、数千から数万nmの二次粒子結晶を超音波や高圧ホモジナイザー、対向衝突型ジェット粉碎機等で微細粒子に粉碎したものが好ましく使用出来る。

【0034】本発明で好ましく使用されるアルミナ水和物は、 $\text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$  ( $n=1\sim 3$ )の構成式で表される。 $n$ が1の場合がペーマイト構造のアルミナ水和物を表し、 $n$ が1より大きく3未満の場合が擬ペーマイト構造のアルミナ水和物を表す。アルミニウムイソプロポキシド等のアルミニウムアルコキシドの加水分解、アルミニウム塩のアルカリによる中和、アルミン酸塩の加水分解等の公知の製造方法により得られる。

【0035】本発明に用いられるアルミナ水和物の一次粒子の平均粒径は、5～50nmが好ましく、より高い光沢を得るためには、5～30nmで平均アスペクト比（平均厚さに対する平均粒径の比）が2以上の平板状の粒子を用いるのが好ましい。

【0036】本発明のインク受容層は目的別に2層以上とするのが好ましく、支持体から離れた最上層のインク受容層は、主として光沢性、耐傷性、および耐候性の向上を目的とし、支持体に近い下層のインク受容層は主として白色性とインク吸収性の向上を目的とする。特に下層のインク受容層には平均一次粒径が5～50nm、好ましくは5～30nmの無機微粒子、および蛍光増白剤を用いることで白色性を高くし、インク溶媒の吸収性を向上させるので好ましい。支持体から離れた上層のイン

(5)

特開2003-285535

9

の経時劣化性、画像部の耐候性、および発色性から好ましい。上層のインク受容層にカチオン性化合物を含有させることでインクの色剤が上層で捕獲されやすく、下層の蛍光増白剤と色剤が接触しにくくなるためと推測される。また、下層に無機微粒子と蛍光増白剤を含有させ、上層のインク受容層の無機微粒子としてアルミナまたはアルミナ水和物を使用することにより白紙部の光沢性が向上するのに加えて、白紙部の経時劣化性、画像部の耐候性、および発色性が向上するので好ましい。上記効果が得られるのは、上層のインク受容層にカチオン性化合物を含有させるかアルミナまたはアルミナ水和物を使用することで上層のインク受容層でインクの色剤が捕獲されやすくなるのに加えて色剤が下層のインク受容層に浸透しにくくなるので下層の蛍光増白剤と色剤の接触がしにくくなることに加え、空気中の微小ガスや光が下層まで届きにくいので下層の蛍光増白剤が劣化しにくくなるためと推測される。好ましくは少なくとも最上層のインク受容層にアスペクト比が2以上のアルミナ水和物を用いることで画像の耐候性や経時ひび割れが改良され、特に下層のインク受容層に平均一次粒径が5～30nmの気相法シリカを用いることでインク吸収性も改良されるので好ましい。平板状アルミナ水和物使用により画像の経時ひび割れが改良される理由は、インク受容層が平板状のアルミナ水和物の積層構造となっているので球状の微粒子と比較して直線状にはひび割れが起きにくいいためと、親水性バインダーがアルミナ水和物の平板状粒子間の界面に集中しやすいために結合強度が高くなるためと推測される。

【0038】本発明で、インク受容層が2層以上の場合の下層のインク受容層は、全固形分量を5～30g/㎡とするのが好ましく、特に10～25g/㎡の範囲が白色度向上効果とインク吸収性からは好ましい。最上層のインク受容層の固形分量は1～15g/㎡の範囲が好ましく、特に1～12g/㎡の範囲がインク吸収性からは好ましい。

【0039】本発明の無機微粒子の平均粒径は、分散された粒子の電子顕微鏡観察により一定面積内に存在する100個の粒子各々の投影面積に等しい円の直径を粒子の粒径として求めた。本発明のアルミナ水和物の一次粒子の平均粒径は、平板状の場合は平面状態にて測定され

10

しく、インク受容層を2層以上とし、最上層に球状粒子を含有させるほうが耐候性、光沢性からは好ましい。球状粒子の平均粒径は最上層のインク受容層の膜厚より大きいことが好ましいが、インク受容層から10μmより大きく突出しないほうが触感からは好ましい。

【0041】本発明では、耐候性を改良する目的で、インク受容層上にコロイダルシリカを主体とした保護層をインク吸収性を低下させない程度、固形分で5g/㎡程度以下で設けても良い。コロイダルシリカは、例えばケイ酸ナトリウムの酸などによる複分解やイオン交換樹脂層を通して得られるシリカゾルを加熱熱成して得られる。コロイダルシリカの一般的な一次粒子の平均粒径は5～100nm程度であり、平均粒径が10～500nm程度の二次粒子を形成しているほうがインク吸収性からは好ましい。市販の球状のものとして日産化学社製、スノーテックス20等、触媒化成工業社製、カタロイドUSB等が挙げられ、鎖状のものとして日産化学社製、スノーテックスUP等が挙げられ、パールネックレス状のものとして日産化学社製、スノーテックスPS-M等が使用出来る。保護層にも本発明のヒドラジン誘導体、含イオウ有機化合物、および糖類の少なくとも1種を含有させてもよい。また、インク受容層の塗布組成物に本発明のヒドラジン誘導体、含イオウ有機化合物、または糖類を添加しないで保護層の塗布組成物のみに添加してインク受容層に浸透させてもよい。

【0042】本発明において、インク受容層で無機微粒子とともに用いられる親水性バインダーとしては、ポリビニルアルコール、澱粉、カルボキシメチルセルロース、ヒドロキシエチルセルロース、ポリエチレンオキサイド、ポリアクリルアミド、ポリビニルピロリドン等、およびこれらの誘導体が挙げられる。特に、ポリビニルアルコールが好ましく、シラノール変性やカチオン変性等の各種変性物も含まれるが、透明性が高くインクのより高い浸透性が得られ、インクの初期の浸透時に膨潤して空隙を塞いでしまわないことが重要であり、この観点から好ましいのは完全または部分ケン化のポリビニルアルコールまたはカチオン変性ポリビニルアルコールである。

【0043】ポリビニルアルコールの中でも特に好ましいのは、ケン化度が80%以上の部分または完全ケン化

(7)

特開2003-285535

11

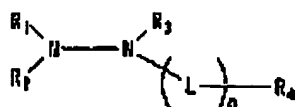
するポリビニルアルコールである。

【0045】本発明において、インク受容層に無機微粒子、親水性バインダー、および蛍光増白剤とともにヒドラジン誘導体、含イオウ有機化合物、および糖類の少なくとも1種を含有させることで耐黄変性と画像の耐光性と耐ガス性が向上する。理由は不明であるが、ヒドラジン誘導体、含イオウ有機化合物、および糖類の少なくとも1種と蛍光増白剤とを用いることにより、各々の特長である白色性、画像の耐候性、耐ガス性が相乗的に向上するのに加えて、蛍光増白剤の欠点である劣化黄変が抑えられ、発色性阻害を抑える色剤の安定化効果が得られるためと推測される。耐水性支持体上に下塗り層、インク受容層、および保護層を設ける場合には、ヒドラジン誘導体、含イオウ有機化合物、および糖類の少なくとも1種を下塗り層、インク受容層、または保護層の少なくとも何れかに含有させても良いが、好ましくは支持体から離れたインク受容層、保護層中にヒドラジン誘導体、含イオウ有機化合物、および糖類の少なくとも1種を含有させ、下塗り層が支持体に近いインク受容層に蛍光増白剤を含有させる。特に、蛍光増白剤を含有する層とヒドラジン誘導体、含イオウ有機化合物、および糖類の少なくとも1種を含有する層を分離する方が耐黄変性、画像の耐候性、および発色性が更に良化するの好ましい。ここで、下塗り層とはポリマー化合物主体が、平均粒径が1 μm以上の比較的大きな無機顔料や有機顔料とポリマー化合物を含有する層である。

【0046】本発明で好ましく使用されるヒドラジン誘導体としては、例えば特開昭61-154989号、特開2001-128984号、同2001-245125号などに記載の化合物がある。うち好ましいものは、下記化1にて表される構造のものである。

【0047】

【化1】



【0048】化1の式中、 $R_1 \sim R_4$ は水素原子、脂肪族基、芳香族基、複素環基を表す。また、 $R_3$ と $R_4$ は互いに連結して環状構造になっていてもよい。うち好ましいものは、 $R_1$ 、 $R_2$ については脂肪族基であり、中でも炭

12

ジノ基については、末端窒素原子が炭素数4以下のアルキル基2つで置換されているもの、またはカルボニル基、オキサリル基、スルホニル基、スルホキシ基、ホスホリル基、イミノメチレン基のいずれかで置換されているものが好ましい。そして以上述べたうち特に好ましいものは、 $R_1$ 、 $R_2$ についてはメチル基であり、 $R_3$ については水素原子、また $R_4$ については炭素数6以下のアルキル基、メトキシ基、ヒドロキシ基のいずれか1つで置換されたアミノ基、末端窒素原子が炭素数4以下のアルキル基2つで置換されたヒドラジノ基、またはカルボニル基で置換されたヒドラジノ基である。

【0049】 $L$ は、カルボニル基、オキサリル基、スルホニル基、スルホキシ基、ホスホリル基、イミノメチレン基を表す。うち好ましいものはカルボニル基、オキサリル基であり、そしてカルボニル基がより好ましい。特に $L$ がカルボニル基で $R_3$ が置換または未置換のヒドラジノ基であるカルボノヒドラジド誘導体、および $L$ がカルボニル基で $R_3$ が置換または未置換のアミノ基であるセミカルバジド誘導体が好ましい。以下に本発明で用いられるヒドラジン誘導体の具体例を示すが、本発明はこれらに限定されるものではない。

【0050】

【化2】

(8)

特開2003-285535

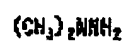
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H1

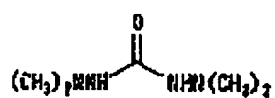
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[0051]

[化3]

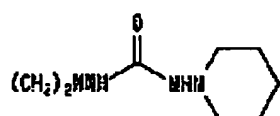


H2

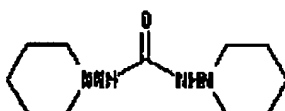


H3

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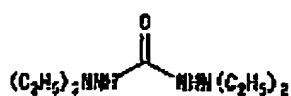


H4

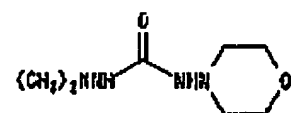


H5

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H6



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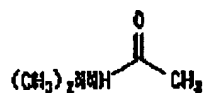
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特開2003-285535

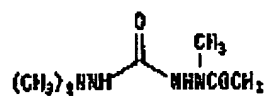
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16

H7



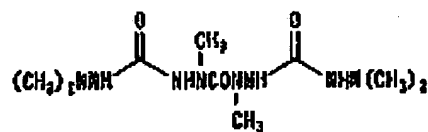
H8



H9



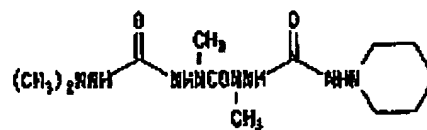
H10



H11



H12



【0052】

【化4】

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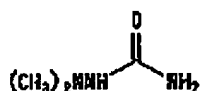
特開2003-285535

17

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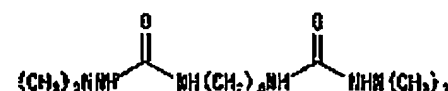
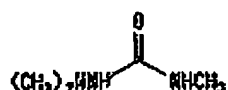
H13

H19



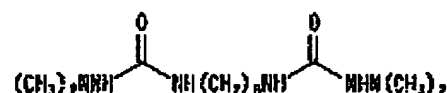
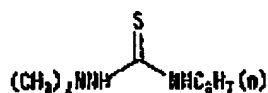
H14

H20



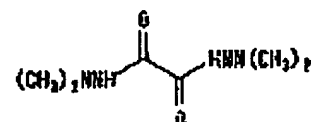
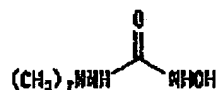
H15

10 H21



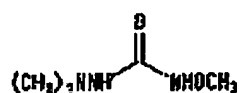
H16

H22



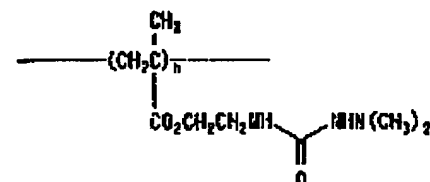
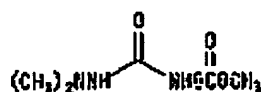
H17

20 H23



H18

H24



【0053】

【化5】

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【0054】本発明のヒドラジン誘導体は、適当な溶剤に添加しても、有機溶剤とともにポリビニルアルコール中に乳化分散して添加してもよい。

【0055】本発明のヒドラジン誘導体をインク受容層へ添加する場合の単位面積当たりの全添加量は、0.01～10g/㎡、好ましくは0.05～3g/㎡である。上記の範囲より少ないと画像の耐久性改良効果が出にくく、多すぎるとインク吸収性が低下したり、画像の

40 経時劣化が早発しやすくなる。

(11)

特開2003-285535

19

ー(2-ヒドロキシエチルチオ)エチル]スルホン、3, 6, 9-トリチオ-1, 11-ウンデカンジオール、4-(メチルチオ)フェノール、2-(フェニルチオ)エタノールが挙げられる。チオウレア系化合物としては、具体的には、チオウレア、N-メチルチオウレア、N-アセチルチオウレア、1, 3-ジフェニルチオウレア、テトラメチルチオウレア、グアニルチオウレア、4-メチルチオセミカルバジド、1, 3-ビス(ヒドロキシメチル)-2(3H)ベンズイミダゾールチオン、6-ヒドロキシ-1-フェニル-3, 4-ジヒドロピリミジン-2(1H)-チオン、1-アリル-2-チオウレア、1, 3-ジメチル-2-チオウレア、1, 3-ジエチル-2-チオウレア、エチレンチオウレア、トリメチルチオウレア、1-カルボキシメチル-2-チオヒダントイン、チオセミカルバジド等が挙げられる。ジスルフィド系化合物は、例えばDL- $\alpha$ -リボ酸、4, 4'-ジチオジモルフォリン、4, 4'-ジチオジブタン酸が好ましい。メルカプト化合物は、チオサリチル酸系等や含窒素複素環化合物が好ましく、例えば、2-メルカプトピリジン、3-ヒドロキシ-2-メルカプトピリジン、2-メルカプトベンズイミダゾール、2-メルカプトイミダゾール、2-メルカプトピリミジン及びそれらの誘導体等が挙げられる。

【0058】本発明で使用される糖類としては、例えば、D-グルコース、D-リボース、マルトース、セロビオース、メリビオース、ゲンチオビオース、D-グルコサミン、D-キシロース、D-ガラクトース、ラクトース、ヒシアノース、ツラノース、ゲンチアノース、ルチノース、L-キシロース、L-ソルボース、D-マニトール、トレハロース、D-フルクトース、スクロース、ラフィノース、スタキオース等の単糖類、少糖類が挙げられる。少糖類はオリゴ糖とも呼ばれ、二糖から十五糖までの重合度の糖質を言う。耐光性、耐ガス性改良の効果からより好ましくはD-グルコース、ラクトース、D-リボース、マルトース、トレハロース等の還元基を有する還元糖が選択される。

【0059】本発明に用いられる蛍光増白剤としては、ビレン誘導体、クマリン誘導体、オキサゾール誘導体、チアゾール誘導体、イミダゾール誘導体、イミダゾロン誘導体、ピラゾリン誘導体およびベンジジン誘導体など

20

【0060】本発明では、全インク受容層に含有される蛍光増白剤の固形分含有量は、インク受容層の単位面積当たりで0.01~2g/㎡、好ましくは0.05~1g/㎡とすることで良好な白色性を有しながら耐黄変、画像の発色性、耐候性の問題の無いインクジェット用記録材料が得られる。特に蛍光増白剤を下層のインク受容層に含有させ、上層のインク受容層には含有させないことが耐黄変、画像の発色性、および耐候性からは好ましい。黄変等に影響を及ぼす蛍光増白剤を下層のインク受容層に含有させることで、空気中の微小ガスや光が下層まで届きにくいので黄変がより緩和されると推測される。

【0061】特に上層のインク受容層に蛍光増白剤を含有させず、下層のインク受容層の塗布液に蛍光増白剤を含有させる方法として親水性バインダー溶液に蛍光増白剤を添加、混合した後で無機微粒子分散液と混合することにより、得られた記録材料の耐黄変性、画像の発色性が更に良好となる。特に親水性バインダーとしては、けん化度80~95%、平均重合度3000~5000のポリビニルアルコールを親水性バインダーの50質量%以上使用するのが好ましい。黄変や画像の耐候性、および発色性に影響を及ぼす蛍光増白剤の保護に加えて上層のインク受容層への移動がさらに抑えられるためと推測される。

【0062】本発明では、インク受容層には親水性バインダーと共に架橋剤(硬膜剤)を用いることが好ましい。架橋剤の具体的な例としては、ホルムアルデヒド、グルタルアルデヒドの如きアルデヒド系化合物、ジアセチル、クロロベンタンジオンの如きケトン化合物、ビス(2-クロロエチル尿素)-2-ヒドロキシ-4, 6-ジクロロ-1, 3, 5-トリアジン、米国特許第3, 288, 775号記載の如き反応性のハロゲンを有する化合物、ジビニルスルホン、米国特許第3, 635, 718号記載の如き反応性のオレフィンを持つ化合物、米国特許第2, 732, 316号記載の如きN-メチロール化合物、米国特許第3, 103, 437号記載の如きイソシアナート類、米国特許第3, 017, 280号、同2, 983, 611号記載の如きアジリジン化合物類、米国特許第3, 100, 704号記載の如きカルボジイミド系化合物類、米国特許第3, 091, 537号記載



(13)

23

節して用いることも可能である。

【0071】本発明に用いられる周期表4A族元素を含む水溶性化合物は水溶性で有れば特に制限はないがチタンまたはジルコニウムを含む水溶性化合物が好ましい。例えばチタンを含む水溶性化合物としては塩化チタン、硫酸チタンが、ジルコニウムを含む水溶性化合物としては酢酸ジルコニウム、塩化ジルコニウム、オキシ塩化ジルコニウム、ヒドロキシ塩化ジルコニウム、硝酸ジルコニウム、塩基性炭酸ジルコニウム、水酸化ジルコニウム、炭酸ジルコニウム・アンモニウム、炭酸ジルコニウム・カリウム、硫酸ジルコニウム、フッ化ジルコニウム化合物等が知られている。これらの化合物はpHが不適当に低い物もあり、その場合は適宜pHを調節して用いることも可能である。本発明に於いて、水溶性とは常温常圧下で水に1重量%以上溶解することを目安とする。

【0072】本発明において、上記水溶性金属化合物のインク受容層中の含有量は、無機微粒子に対して0.1～10重量%が好ましく、更に好ましくは1～5重量%である。

【0073】本発明のインク受容層で使用されるカチオン性ポリマーとしては、ポリエチレンイミン、ポリジアリルアミン、ポリアリルアミン、アルキルアミン重合物、特開昭59-20696号、同59-33176号、同59-33177号、同59-155088号、同60-11389号、同60-49990号、同60-83882号、同60-109894号、同62-198493号、同63-49478号、同63-115780号、同63-280681号、特開平1-40371号、同6-234268号、同7-125411号、同10-193776号公報等に記載された1～3級アミノ基、4級アンモニウム塩基を有するポリマーが好ましく用いられる。これらのカチオンポリマーの分子量は、5,000以上が好ましく、更に5,000～10万程度が好ましい。

【0074】これらのカチオン性ポリマーの使用量は画像のひび割れからは少ない方が好ましく、無機微粒子に対して1～7重量%、好ましくは2～5重量%である。

【0075】本発明で好ましくは、インクジェット用記録材料を構成する少なくとも1層、より好ましくは少なくとも1層のインク受容層にはメチロールアミノ系化合物

特開2003-285535

24

られ、それらの中から1種以上が使用される。本発明の画像の経時ひび割れ防止効果からはメチロールメラミン系化合物が好ましく使用される。インク受容層へ添加する場合の添加量は、親水性バインダーの固形分に対して0.5～50重量%であり、好ましくは1～30重量%である。少なすぎると画像のひび割れ改良効果は得られず、多すぎるとインク吸収性が低下する。インクジェット用記録材料の各層に添加する場合もインク受容層と同様の添加量が好ましい。

【0076】本発明により印字画像の経時でのひび割れが改良される理由は不明であるが、インク受容層に各材料を添加する場合について以下のように推測される。即ち、インク受容層にヒドラジン誘導体、含イオウ有機化合物、および糖類の1種以上を含有させることで親水性バインダー同士の水素結合等や、無機微粒子と新素市営バインダーとの結合が阻害されており、印字することでインク中の水や有機溶剤により更に結合力が弱くなってひび割れが発生しやすくなっているが、メチロールアミノ系化合物の使用、好ましくは含ホウ素化合物と併用することで、親水性バインダーの水酸基等や無機微粒子の活性基との結合、またはそれらの結合を促進することでヒドラジン誘導体等による親水性バインダー同士や無機微粒子と親水性バインダーとの結合の阻害を抑えると推測され、メチロールアミノ系化合物、および含ホウ素化合物に加えて更に水溶性金属化合物が存在することにより、それらの結合数が増加し、結合力が更に強化されることにより、空気中やインク中の水等の溶剤により結合力が低下せず、温度や湿度が変化しても画像にひび割れが発生しにくくなると推測される。特にメチロールアミノ系化合物としてはメチロールメラミン系化合物が好ましく、更にインク受容層用の塗工液のpHを3.5～6.0とし、インク受容層に加熱処理等で50℃以上の温度をかけることでメチロール基と親水性バインダーや無機微粒子の活性基との反応性が上がり、インク受容層の未印字部の高温ひび割れや画像の経時ひび割れが良化すると推測される。更にインク受容層を2層以上とすることで歪みが小さくなるためか単層よりも画像の経時ひび割れが良化する。

【0077】本発明のインク受容層にメチロールアミノ系化合物を含有させる場合には、例えば、無機微粒子、

(14)

25

法、またはメチロールアミノ系化合物を除いたインク受容層用の主液に塗工直前にメチロールアミノ系化合物含有液を添加し、混合後に塗工する方法が好ましく、特にインク受容層用の主液を送液中のインラインでメチロールアミノ系化合物含有液を添加し、混合する方法が、画像の経時ひび割れがより向上するので好ましい。その理由としてはメチロールアミノ系化合物の活性劣化が少なく、塗工液中に均一混合されるのでメチロールアミノ系化合物とポリビニルアルコールや無機微粒子との結着数が多くなり、強くなるためと推測される。ここで塗工直前とは一般的に塗工する数分前から数秒前である。2液を添加後に使用する混合装置としては、例えばインラインミキサー、スタチックミキサー等がKenics社、Sulger社、晃立社、東レ社より市販されている装置が使用出来る。また、メチロールアミノ系化合物含有の塗工液を塗工した後の減率乾燥以降の乾燥工程でインク受容層の表面温度を50℃以上、好ましくは60℃以上にすることで高温ひび割れや印字画像の経時でのひび割れが更に良化する。乾燥工程でインク受容層の水分が10質量%程度以下まで乾燥させた後、記録材料原反を巻き取るまでの工程や、巻き取った後の記録材料原反を別ラインでインク受容層の表面温度が50℃以上になる加温工程を行うことでも高温ひび割れや印字画像の経時によるひび割れが改良される。加温工程の環境温度は加温時間によるが、記録材料の経時劣化が起きない温度である150℃以下、特に100℃程度以下が好ましい。加温する時間は温度により変化するが、数秒から数時間が適当である。乾燥工程直前に冷却工程により塗工されたインク受容層用の塗工液を20℃程度以下、好ましくは15℃以下に冷却することで乾燥時の風紋の発生を抑えられるので好ましい。

【0078】本発明において、インク受容層には更に、界面活性剤、着色染料、着色顔料、インク染料の定着剤、紫外線吸収剤、酸化防止剤、耐水化剤、顔料の分散剤、消泡剤、レベリング剤、防腐剤、粘度安定剤などの公知の各種添加剤を添加することもできる。

【0079】本発明のインク受容層には、更に皮膚の脆\*

<下引き層>

石灰処理ゼラチン

スルフォコハク酸-2-エチルヘキシルエステル塩

特開2003-285535

26

\* 弱性を改良するために各種油滴を含有することができ、そのような油滴としては室温における水に対する溶解性が0.01質量%以下の疎水性高沸点有機溶媒（例えば、流動パラフィン、ジオクチルフタレート、トリクレジルホスフェート、シリコンオイル等）や重合体粒子（例えば、スチレン、ブチルアクリレート、ジビニルベンゼン、ブチルメタクリレート、ヒドロキシエチルメタクリレート等の重合性モノマーを一種以上重合させた粒子）を含有させることができる。そのような油滴は好ましくは親水性バインダーに対して10～50質量%の範囲で用いることができる。

【0080】本発明において、インク受容層の塗布方法、および下塗り層、保護層を設ける場合の塗布方法は、特に限定されず、公知の塗布方法を用いることができる。例えば、スライドビード方式、カーテン方式、エクストルージョン方式、エアナイフ方式、ロールコーティング方式、ロッドバーコーティング方式等がある。

【0081】

【実施例】以下、実施例により本発明を詳しく説明するが、本発明の内容は実施例に限られるものではない。なお、部とは固形分質量部を意味する。

【0082】実施例1

支持体として、LBKP（50部）とLBSP（50部）のバルブ配合からなる170g/㎡の基紙の表面に低密度ポリエチレン（70部）と高密度ポリエチレン（20部）と酸化チタン（10部）からなる樹脂組成物を25g/㎡溶融押し出し塗布しておもて面樹脂被覆層を設け、裏面に高密度ポリエチレン（50部）と低密度ポリエチレン（50部）からなる樹脂組成物を25g/㎡溶融押し出し塗布して裏面樹脂被覆層を設けた樹脂被覆紙を用意した。

【0083】上記樹脂被覆紙のおもて面樹脂被覆層に高周波コロナ放電処理を施した後、下記組成の下引き層をゼラチンが50mg/㎡となるように塗布乾燥して支持体を作成した。尚、部とは、質量部を表す。

【0084】

100部

2部

(15)

特開2003-285535

27	28
ジメチルジアリルアンモニウムクロライドホモポリマー	4部
(第一工業製薬(株)製、シロ-4DC902P、分子量9000)	
ポリビニルアルコール	26部
(商品名:PVA235、(株)カネミ製、けん化度88%、平均重合度3500)	
蛍光増白剤	1部
(商品名:UVITEX BAC、チバ・ファルザイ・ケミカル社製)	
ほう酸	5部
両性界面活性剤	0.3部
(商品名:SNAM AM-2150、日本イーファグメント社製)	

【0087】

10

&lt;上層のインク受容層用塗布組成物1&gt;

気相法シリカ	100部
(平均一次粒径7nm、BET法による比表面積300m <sup>2</sup> /g)	
ジメチルジアリルアンモニウムクロライドホモポリマー	4部
(第一工業製薬(株)製、シロ-4DC902P、分子量9000)	
ポリビニルアルコール	20部
(商品名:PVA235、(株)カネミ製、けん化度88%、平均重合度3500)	
ほう酸	5部
両性界面活性剤	0.3部
(商品名:SNAM AM-2150、日本イーファグメント製)	
水溶性金属化合物:塩基性ポリ水酸化アルミニウム	4部
(商品名:ビュラケムMT、理研グリーン社製)	
化2の化合物(H1)	5部
メチロールメラミン系化合物	2部
(住友化学社製、スミレーズレジン613)	

【0088】実施例2

実施例1でインク受容層組成の化2の化合物(H1)に代えて化2の化合物(H3)を用いた以外は実施例1と同様にして実施例2のインクジェット用記録材料を得た。

【0089】実施例3

実施例1でインク受容層組成の化2の化合物(H1)に代えて化4の化合物(H16)を用いた以外は実施例1と同様にして実施例3のインクジェット用記録材料を得た。

【0090】実施例4

実施例1でインク受容層組成の化2の化合物(H1)に代えて化5の化合物(H20)を用いた以外は実施例1と同様にして実施例4のインクジェット用記録材料を得た。

【0093】実施例7

実施例1でインク受容層組成の化2の化合物(H1)に代えて3-ヒドロキシ-2-メルカプトピリジンを用いた以外は実施例1と同様にして実施例7のインクジェット用記録材料を得た。

【0094】実施例8

実施例1でインク受容層組成の化2の化合物(H1)に代えてD-グルコースを用いた以外は実施例1と同様にして実施例8のインクジェット用記録材料を得た。

【0095】実施例9

実施例1で上層のインク受容層用塗布組成物の水溶性金属化合物に代えてカチオン性ポリマー(豊田化工社製、ジェットフィックス30)を使用した以外は実施例1と同様にして実施例9のインクジェット用記録材料を得た。

(16)

特開2003-285535

29

30

実施例1で上層のインク受容層から測定した膜面pHが5.8になるように水酸化カリウム溶液で調整した以外は実施例1と同様にして実施例12のインクジェット用記録材料を得た。

#### 【0099】実施例13

実施例1で上層のインク受容層から測定した膜面pHが3.1になるように硝酸溶液で調整した以外は実施例1と同様にして実施例13のインクジェット用記録材料を得た。

#### 【0100】実施例14

実施例1で上層のメチロールメラミン系化合物を抜いた以外は実施例1と同様にして実施例14のインクジェット用記録材料を得た。

#### \*【0101】実施例15

実施例1で、下層、および上層のインク受容層用塗布組成物1を下記の下層、および上層のインク受容層用塗布組成物2に代え、下層の気相法シリカを固形で15g/㎡、上層のアルミナ水和物を固形で9g/㎡、となるように同時塗布、乾燥して実施例15のインクジェット用記録材料を得た。上層のインク受容層から測定した膜面pHが4.0になるように水酸化カリウム溶液で調整した。下層のインク受容層用塗布組成物2調整時に、蛍光増白剤はポリビニルアルコール溶液に添加、混合した後で気相法シリカ分散液に添加した。

#### 【0102】

#### <下層のインク受容層用塗布組成物2>

気相法シリカ	100部
(平均一次粒径12nm、BET法による比表面積200㎡/g)	
ジメチルジアリルアンモニウムクロライドホモポリマー	4部
(第一工業製薬(株)製、シャトルDC902P、分子量9500)	
ほう酸	3部
ポリビニルアルコール	15部
(商品名:PVA235、(株)三井製、けん化度88%、平均重合度3500)	
蛍光増白剤	1部
(商品名:UVITEX BAC、チカ・ソバシヤリテイ・ナミカス社製)	
両性界面活性剤	0.3部
(商品名:SWAM AM-2150、日本イソフラグメント社製)	

#### 【0103】

#### <上層のインク受容層用塗布組成物2>

アルミナ水和物	100部
(平均一次粒径14nm、アスペクト比5の平板状粒子)	
硝酸	1部
ほう酸	0.5部
ポリビニルアルコール	15部
(商品名:PVA235、(株)三井製、けん化度88%、平均重合度3500)	
界面活性剤	0.5部
化2の化合物(H1)	5部
メチロールメラミン系化合物	2部
(住友化学社製、スミレーズレジン613)	

#### 【0104】実施例16

実施例1でインク受容層を下記の実施例16のインク受容層用塗布組成物3を用い、気相法シリカの固形分塗布量を2.2g/

※尚、インク受容層用塗布組成物3調整時に、蛍光増白剤はポリビニルアルコール溶液に添加、混合した後で気相法シリカ分散液に添加した。



(17)

特開2003-285535

31

32

(商品名: UVITEX BAC, 株式会社「ユニバーサル」製)

ほう酸

5部

両性界面活性剤

0.3部

(商品名: SWAM AM-2150, 日本イソナク製)

水溶性金属化合物: 塩基性ポリ水酸化アルミニウム

4部

(商品名: ビュラムMT, 理研グリーン製)

化2の化合物(H1)

2.1部

メチロールメラミン系化合物

2部

(住友化学社製, スミレーズレジン613)

## 【0106】実施例17

実施例16で下層のインク受容層で使用する蛍光増白剤をUVITEX BACからUVITEXBA (株式会社「ユニバーサル」製)に代えた以外は実施例16と同様にして実施例17インクジェット用記録材料を得た。

## 【0107】実施例18

実施例17で上層のインク受容層で使用する化2の化合物(H1)を抜いた以外は実施例1と同様にして実施例18インクジェット用記録材料を得た。

## 【0108】実施例19

実施例15で上層のインク受容層で使用する化2の化合物(H1)を抜いた以外は実施例15と同様にして実施例19インクジェット用記録材料を得た。

## 【0109】比較例1

実施例16でインク受容層から蛍光増白剤とメチロールメラミン系化合物を抜いた以外は実施例16と同様にして比較例1のインクジェット用記録材料を得た。

## 【0110】比較例2

実施例16でインク受容層から化2の化合物(H1)とメチロールメラミン系化合物を抜いた以外は実施例16と同様にして比較例2のインクジェット用記録材料を得た。

## 【0111】比較例3

実施例16でインク受容層から蛍光増白剤、化2の化合物(H1)、水溶性金属化合物、およびメチロールメラミン系化合物を抜いた以外は実施例16と同様にして比較例3のインクジェット用記録材料を得た。

【0112】得られた各々のインクジェット用記録材料について、23℃、50%RHで一旦夜経過後、下記により、白色性、耐黄変性、インク吸収性、印字後の画像保存性(耐光性および耐ガス性)、および画像の色鮮

10 較し、下記の基準で評価した。

○:殆ど変化無し。

△:やや変化有る。

×:変化が大きい。

【0115】<インク吸収性>インクジェットプリンター(セイコーエプソン社製PM-800C)を用いて、C、M、Yをそれぞれ100%で印字して、印字直後にPPC用紙を印字部に重ねて軽く圧着し、PPC用紙に転写したインク量の程度を目視で観察し、下記の基準で評価した。

○:全く転写しない。

△:やや転写するが実使用可。

×:転写し実使用不可。

【0116】<耐光性>インクジェットプリンター(セイコーエプソン社製PM-800C)を用いてCYMKのインクでそれぞれベタ印字を行い、アトラス社製サンテストCPS光退色試験機にて600W/m<sup>2</sup>で50時間照射した後、印字部の濃度を測定し、画像残存率(照射後濃度/照射前の濃度)を求め、CMYK画像の内、最も残存率が低いものを表示した。

【0117】<耐ガス性>上記耐光性試験と同様に印字後、室内壁面に室温で100日間曝露した後、印字部の濃度を測定し、画像残存率(曝露後濃度/曝露前の濃度)を求め、CMYK画像の内、最も残存率が低いものを表示した。

【0118】<発色性>各記録材料にインクジェットプリンター(セイコーエプソン社製PM-800C)を用いてC、G、Y、R、M、Bのベタ印字を行い、各々のJIS-Z8730で規定されるa\*、b\*のデータをa\*-b\*座標に記入し、各点を直線で結んで囲まれた面積と比較した。面積が広いほうが発色性は良好であり、比

(18)

特開2003-285535

33

34

○：全くひび割れ無し。

\*【0120】

△：一部に微細なひび割れ有るが実使用で問題無し。

【表1】

×：全面にひび割れ有り。

\*

	白色性	耐黄変性	インク 吸収性	保存性(%) 耐光性	耐ガス性	発色性	画像部 ひび割れ
実施例1	⊕	○	○	88	90	○	○
実施例2	⊕	○	○	89	90	○	○
実施例3	⊕	○	○	90	92	○	○
実施例4	⊕	○	○	88	91	○	○
実施例5	⊕	○	○	87	91	○	○
実施例6	⊕	△	○	85	90	○	○
実施例7	⊕	△	○	85	88	△	○
実施例8	⊕	△	○	84	86	○	○
実施例9	⊕	○	○	85	88	○	○
実施例10	⊕	○	○	90	91	○	○
実施例11	○	○	○	85	87	○	○
実施例12	⊕	△	○	89	87	○	○
実施例13	⊕	△	○	85	91	○	○
実施例14	⊕	○	○	87	90	○	△
実施例15	⊕	○	○	86	88	○	○
実施例16	○	△	○	84	86	△	○
実施例17	△	△	○	85	87	△	○
実施例18	⊕	○	○	80	73	○	○
実施例19	⊕	○	○	81	74	○	○
比較例1	×	△	○	87	90	△	×
比較例2	○	×	○	75	69	△	△
比較例3	×	△	○	76	71	○	△

【0121】光沢度は、いずれの記録材料も高い光沢性を有していた。

【0122】上記結果から明らかなように実施例1～19の記録材料は良好な特性を示した。実施例16で下層のインク受容層から紫外光増白剤とメチロールメラミン系化合物を抜いた比較例1の記録材料は、白色性と画像の経時ひび割れに劣った。実施例16でインク受容層のヒドラジン誘導体とメチロールメラミン系化合物を抜いた比較例2は、耐黄変性、画像の耐光性と耐ガス性が大き

く低下した。実施例16でヒドラジン誘導体、水溶性金属化合物、およびメチロールメラミン系化合物を抜いた比較例3は、発色性は良好であるが、白色性、画像の耐光性と耐ガス性が大きく低下した。

【0123】

【発明の効果】本発明によれば、光沢性、白色性、およびインク吸収性が良好で、画像の耐候性と発色性に優れたインクジェット用記録材料が得られる。

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【手続補正書】

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【手続補正 1】

【補正対象書類名】 明細書

【補正対象項目名】 特許請求の範囲

【補正方法】 変更

【補正の内容】

【特許請求の範囲】

【請求項 1】

耐水性支持体上に少なくとも 1 層の無機微粒子、および親水性バインダーを含有するインク受容層を有するインクジェット用記録材料において、該インクジェット用記録材料が、蛍光増白剤を含有し、更に、ヒドラジン誘導体、含イオウ有機化合物、および糖類の少なくとも 1 種を含有することを特徴とするインクジェット用記録材料。

【請求項 2】

前記インク受容層が 2 層以上であり、前記支持体に近いインク受容層が蛍光増白剤を含有し、前記支持体から離れたインク受容層がヒドラジン誘導体、含イオウ有機化合物、および糖類の少なくとも 1 種を含有することを特徴とする請求項 1 に記載のインクジェット用記録材料。

【請求項 3】

耐水性支持体上に少なくとも 2 層の無機微粒子、および親水性バインダーを含有するインク受容層を有するインクジェット用記録材料において、該支持体に近いインク受容層が蛍光増白剤の少なくとも 1 種を含有しており、該支持体から離れたインク受容層がカチオン性化合物を含有していることを特徴とするインクジェット用記録材料。

【請求項 4】

耐水性支持体上に少なくとも 2 層の無機微粒子、および親水性バインダーを含有するインク受容層を有するインクジェット用記録材料において、該支持体に近い、および前記受容層が

# PATENT ABSTRACTS OF JAPAN

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(21)Application number : 2002-088869 (71)Applicant : MITSUBISHI PAPER  
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## (54) INK JET RECORDING MATERIAL

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an ink jet recording material which is good in a gloss, a white property and an ink absorptive property and excellent in weather resistance of an image and a coloring property.

SOLUTION: For the ink jet recording material having at least one layer of an ink receptive layer on a waterproof base material, the ink receptive layer contains an inorganic fine particle, a hydrophilic binder and a fluorescent brightner and further contains a hydrazine derivative, a sulfur compound and at least one kind of saccharides. Especially the ink receptive layer is formed of at least two layers, and the lower layer near a waterproof base material contains the fluorescent brightner and the upper layer apart from the waterproof base material contains the hydrazine derivative, the sulfur compound and at least one kind of the saccharides.

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examiner's decision of rejection]

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## CLAIMS

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[Claim(s)]

[Claim 1] The record ingredient for ink jets characterized by for this record ingredient for ink jets containing a fluorescent brightener in the non-subtlety particle of at least one layer, and the record ingredient for ink jets which has an ink absorbing layer containing a hydrophilic binder, and containing at least one sort of a hydrazine derivative, a \*\* sulfur organic compound, and a saccharide further on a waterproof base material.

[Claim 2] The record ingredient for ink jets according to claim 1 with which the ink absorbing layer which said ink absorbing layer is more than two-layer, and the ink absorbing layer near said base material contained the fluorescent brightener, and is distant from said base material is characterized by containing at least one sort of a hydrazine derivative, a \*\* sulfur organic compound, and a saccharide.

[Claim 3] The record ingredient for ink jets characterized by for the ink absorbing layer near this base material containing at least one sort of a fluorescent brightener, and the ink absorbing layer distant from this base material containing the cationic compound in the record ingredient for ink jets which has an ink absorbing layer containing a two-layer non-subtlety particle and a two-layer hydrophilic binder at least on a waterproof base material.

[Claim 4] The record ingredient for ink jets with which the non-subtlety particle of the ink absorbing layer which the ink absorbing layer near this base material contained at least one sort of a fluorescent brightener in the record ingredient for ink jets which has an ink absorbing layer containing at least a two-layer non-subtlety particle and a two-layer hydrophilic binder, and is distant from this base material is characterized by being at least one sort of an alumina and hydrated alumina on a waterproof base material.

[Claim 5] The record ingredient for ink jets according to claim 3 or 4 with which the ink absorbing layer distant from said base material is characterized by containing at least one sort of a hydrazine derivative, a \*\* sulfur organic compound, and a saccharide.

[Claim 6] The record ingredient for ink jets according to claim 1, 2, or 5 said whose hydrazine derivative is at least one sort of a carbonohydrazide derivative and a semicarbazide derivative.

[Claim 7] The record ingredient for ink jets given in any 1 term of claims 1-6 said whose fluorescent brighteners are cationic organic fluorescent brighteners.

[Claim 8] The record ingredient for ink jets according to claim 3 characterized by the cationic compounds of an ink absorbing layer which are separated from said base material being water-soluble metallic compounds.

[Claim 9] The record ingredient for ink jets given in any 1 term of claims 1-8 which are at least one sort of a gaseous-phase method [ said non-subtlety particle is the first / an average of / particle size of 5-30nm ] silica, an alumina, and hydrated alumina.

[Claim 10] The record ingredient for ink jets given in any 1 term of claims 2-9 characterized by for the ink absorbing layer near said base material containing 80 - 95%

of saponification degrees, and a mean molecular weight containing the polyvinyl alcohol or its denaturation object of 3000-5000.

[Claim 11] The record ingredient for ink jets given in any 1 term of claims 2-10 characterized by the ink absorbing layer distant from said base material not containing the fluorescent brightener.

[Claim 12] The record ingredient for ink jets given in any 1 term of claims 1-11 characterized by said ink absorbing layer containing the methylol amino system compound.

## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention has high gloss and white nature, and relates to xanthochroism-proof, the color enhancement of a printing image, a crack, and the record ingredient for ink jets with good weatherability in more detail about the record ingredient for ink jets with good ink absorptivity.

[0002]

[Description of the Prior Art] The record ingredient which comes to prepare the ink absorbing layer of the porosity which consists pigments, such as amorphous silica, of water-soluble binders, such as polyvinyl alcohol, on the base material called usual paper and a usual ink jet record form as a record ingredient used for an ink jet recording method is known.

[0003] For example, the record ingredient which applies silicon-containing pigments, such as a silica, to JP,55-51583,A, 56-157, 57-107879, 57-107880, 59-230787, 62-160277, 62-184879, 62-183382, a 64-11877 official report, etc. with a drainage system binder like disclosure at a paper base material, and is obtained is proposed.

[0004] Moreover, using the synthetic silica particle (a gaseous-phase method silica being called henceforth) by the gaseous-phase method for official reports, such as JP,3-56552,B, JP,2-188287,A, this common one No. 81064 [ ten to ], this common one No. 119423 [ ten to ], this common one No. 175365 [ ten to ], this common one No. 193776 [ ten to ], 10-203006, 10-217601, this common one No. 20300 [ 11 to ], this common one No. 20306 [ 11 to ], and this common No. 34481 [ 11 to ] official report, is indicated. Moreover, the record ingredient which used an alumina and hydrated alumina for JP,62-174183,A, JP,2-276670,A, JP,5-32037,A, JP,6-199034,A, etc. is indicated. The mean particle diameter of a primary particle is an ultrafine particle dozens of nm or less, and the hydrated alumina currently indicated, an alumina, and a gaseous-phase method silica have the description that high gloss and high ink absorptivity are acquired.

[0005] On the other hand, as a base material of the record ingredient for ink jets, generally paper is used and was giving a role of an ink absorbing layer conventionally to the paper itself. While a photograph-like record sheet is demanded in recent years, the record sheet using a paper base material has the problem of the cock ring after gloss, texture, a water resisting property, and printing (a wrinkle or flapping) etc., and the paper base material by which waterproof processing was carried out, for example, the resin laminated paper which laminated polyolefin resin, such as polyethylene, to both sides of paper, (polyolefin resin coat paper), a plastic film, etc. have come to be used. However,

since a waterproof base material cannot absorb ink unlike a paper base material, the ink absorptivity of the ink absorbing layer prepared on the base material is important for it, and it needs to raise the voidage of an ink absorbing layer. Therefore, coverage of non-subtlety particles, such as a gaseous-phase method silica, needed to be made [ many ], and the ratio of the binder to a non-subtlety particle needed to be reduced further.

[0006] However, non-subtlety particles, such as a gaseous-phase method silica, are used for an ink absorbing layer by the high ratio, and the porosity record ingredient which lowered the ratio of a binder has the problem of being easy to discolor the blank paper section during storage. that is, the plasticizer and antioxidant of the film origin by which the ink absorbing layer was adsorbed at the time of the preservation in a file etc. yellow by oxidizing by light, heat, the minute amount gas in atmospheric air, etc. (the following and a file -- it is described as yellowing). moreover, it is because the binder of content, a surfactant, a mordant, a pigment, etc. deteriorate by light, heat, the minute amount gas in atmospheric air, etc. in an ink absorbing layer from the first -- it yellows (the following and degradation -- it is described as yellowing).

[0007] JP,7-68920,A -- yellowing -- the record sheet which has the porosity ink absorbing layer which contains a fluorescent brightener for prevention is indicated. However, since the fluorescent brightener itself was unstable, it was easy to generate yellowing by own degradation, and the lightfastness of an image also became a lowering inclination. yellowing by specific lamination and a specific additive although the record object which at least one layer of a recording layer contained at least one sort of a coloring agent and fluorescent dye, mean particle diameter contained the pigment 1 micrometer or less for feeling of \*\* white nature amelioration, and opacity made 50% or less is indicated by JP,2000-211247,A -- amelioration and color enhancement are not indicated. although the record medium which has the porosity ink absorbing layer of fluorescent brightener content, and makes the front face pH by the side of an ink absorbing layer 6.5 or less [ 4.5 or more ] is indicated by JP,2001-246833,A in order to control yellowing at the time of preservation -- degradation -- yellowing to yellowing, it is inadequate and according to specific lamination and a specific additive -- amelioration and weatherproof amelioration of an image are not indicated.

[0008] Moreover, since lightfastness gets worse even if there is gas-proof nature which prevents fading by minute amount gas and which is effectiveness, or gas-proof nature gets worse even if lightfastness becomes good when the porosity ink absorbing layer which consists of a non-subtlety particle is made to contain the compound known as the fading inhibitor of the printing image by minute amount gas, and a light-fast amelioration agent, there are very few compounds which improve both gas-proof nature and lightfastness. Moreover, in adding the fading inhibitor of the printing image by minute amount gas, and a light-fast amelioration agent to a porous ink absorbing layer, it has the inclination to make the crack in the passage of time of a printing image promote in ink.

[0009] although the proposal which improves gas-proof nature by making the porosity ink absorbing layer which consists of pseudo-boehmite contain a thiourea derivative is made by JP,8-25796,A, it is based on concomitant use with lamination or a fluorescent brightener -- -proof -- yellowing -- there is no publication about amelioration or image shelf-life amelioration. although it is indicated by JP,61-154989,A that lightfastness is improved by making the ink absorbing layer which consists of a synthetic silica contain a hydrazide compound, aggravation of gas-proof nature feels uneasy -- having -- -proof --

there was also no publication about yellowing, and when a hydrazide system compound was used to a porosity ink absorbing layer, there was an inclination which the crack in the passage of time of a printing image tends to generate in ink. concomitant use with a fluorescent brightener, and yellowing by lamination although the proposal which prevents yellowing of a blank paper part by making a porosity ink acceptance layer contain at least one sort of a urea derivative, a semicarbazide derivative, KARUBO hydrazide derivative, and a hydrazine derivative is made by JP,7-314881,A -- there are not prevention and a publication about the weatherability of an image.

[0010]

[Problem(s) to be Solved by the Invention] Furthermore, this invention persons found out that color enhancement tends to fall to the ink absorbing layer which used the fluorescent brightener as a problem at the time of printing by the ink jet in addition to weatherproof lowering of an image.

[0011] Therefore, it has high glossiness and white nature, and ink absorptivity is good, and passes, yellowing of the blank paper section by the time cannot take place easily, and the object of this invention has the weatherability of the printed image section, and color enhancement in offering the good record ingredient for ink jets.

[0012]

[Means for Solving the Problem] As a result of this invention persons' examining many things about the above-mentioned technical problem, the object of this invention was mainly attained by the following means.

[0013] (1) The record ingredient for ink jets with which this record ingredient for ink jets is characterized by containing a non-subtlety particle, a hydrophilic binder, and a fluorescent brightener, and containing at least one sort of a hydrazine derivative, a \*\* sulfur organic compound, and a saccharide further in the record ingredient for ink jets which has the ink absorbing layer of at least one layer on a waterproof base material.

[0014] (2) The record ingredient for ink jets given in the above (1) with which the ink absorbing layer which said ink absorbing layer is more than two-layer, and the ink absorbing layer near said base material contained the fluorescent brightener, and is distant from said base material is characterized by containing at least one sort of a hydrazine derivative, a \*\* sulfur organic compound, and a saccharide.

[0015] (3) The record ingredient for ink jets characterized by for the ink absorbing layer near this base material containing at least one sort of a fluorescent brightener, and the ink absorbing layer distant from this base material containing the cationic compound in the record ingredient for ink jets which has an ink absorbing layer containing a two-layer non-subtlety particle and a two-layer hydrophilic binder at least on a waterproof base material.

[0016] (4) The record ingredient for ink jets with which the non-subtlety particle of the ink absorbing layer which the ink absorbing layer near this base material contained at least one sort of a fluorescent brightener in the record ingredient for ink jets which has an ink absorbing layer containing at least a two-layer non-subtlety particle and a two-layer hydrophilic binder, and is distant from this base material is characterized by being at least one sort of an alumina and hydrated alumina on a waterproof base material.

[0017] (5) The record ingredient for ink jets given in any of aforementioned (1) - (4) said whose fluorescent brightener is a cationic organic fluorescent brightener they are.

[0018] (6) The record ingredient for ink jets given in any of aforementioned (1) - (5)



characterized by the ink absorbing layer distant from said waterproof base material not containing the fluorescent brightener they are.

[0019] (7) The record ingredient for ink jets given in any of aforementioned (1) - (6) characterized by said ink absorbing layer containing the methylol amino system compound they are.

[0020]

[Embodiment of the Invention] Hereafter, this invention is explained to a detail. As a waterproof base material used for this invention, the resin coat paper which laminated polyolefin resin is mentioned to at least one side of plastic resin films, such as polyester resin, such as polyethylene terephthalate, diacetate resin, triacetate resin, acrylic resin, polycarbonate resin, a polyvinyl chloride, polyimide resin, cellophane, and celluloid, and paper. The thickness of the waterproof base material used for this invention has desirable about about 50-300 micrometers.

[0021] Although the paper which especially a limit does not have the stencil which constitutes the resin coat paper preferably used in this invention, and is generally used can be used, a smooth stencil which is used for the base material for photographs more preferably is desirable. as the pulp which constitutes a stencil -- natural pulp, playback pulp, a synthetic pulp, etc. -- one sort -- or two or more sorts are mixed and it is used. Additives, such as the sizing compound generally used of paper making, a paper reinforcing agent, a loading material, an antistatic agent, a fluorescent brightener, and a color, are blended with this stencil.

[0022] Furthermore, surface spreading of a surface sizing compound, a surface paper durability agent, a fluorescent brightener, an antistatic agent, a color, the anchoring agent, etc. may be carried out.

[0023] Moreover, although there is especially no limit about the thickness of a stencil, the good thing of the surface smooth nature which impressed paper under paper milling or in the calender after paper milling, and compressed the pressure is desirable, and the basis weight has desirable 30 - 250 g/m<sup>2</sup>. However, the consistency of a stencil is 0.6 - 1.05 g/cm<sup>3</sup> preferably three or less 1.10 g/cm for stiffness. If a consistency is too small, even if it will perform a resin coat, uniform surface smooth nature is hard to be obtained.

[0024] As resin of resin coat paper, the resin hardened with polyolefin resin or an electron ray can be used. As polyolefin resin, it is the copolymers which consist or more of two of olefins, such as a homopolymer of olefins, such as low density polyethylene, high density polyethylene, polypropylene, polybutene, and the poly pentene, or ethylene propylene rubber, and such mixture, and the thing of various kinds of consistencies and a melt viscosity characteristic (melt index) can be independently used for them, mixing.

[0025] In the resin of resin coat paper, moreover, white pigments, such as titanium oxide, a zinc oxide, talc, and a calcium carbonate, Fatty-acid amides, such as octadecanamide and an arachidic acid amide, zinc stearate, Fatty-acid metal salts, such as calcium stearate, aluminum stearate, and magnesium stearate, Antioxidants, such as IRUGA NOx 1010 and IRUGA NOx 1076, Blue pigments and colors, such as cobalt blue, ultramarine blue, sicilian blue, and a copper phthalocyanine blue, It is desirable to add combining suitably various kinds of additives, such as a pigment of Magentas, such as cobalt violet, fast violet, and manganese purple, a color, a fluorescent brightener, and an ultraviolet ray absorbent.

[0026] In the case of polyolefin resin, it is manufactured by the so-called extrusion

coating method which casts the resin which carried out heating fusion on the stencil it runs, and, as for the resin coat paper which is the base material preferably used in this invention, the right face or both sides are covered with resin. Moreover, after applying resin by coating machines generally used, such as a gravure coating machine and a blade coating machine, in the case of the resin hardened with an electron ray, an electron ray is irradiated, it stiffens resin, and is covered. Moreover, before covering resin in a stencil, it is desirable to perform activation, such as corona discharge treatment and flame treatment, to a stencil. The field (right face) where the ink absorbing layer of a base material is applied is processed on a glossy surface, a mat side, etc. according to the application. It is more desirable to carry out a resin coat from the point of curl prevention, although it is not necessary to cover resin at the rear face. A rear face is usually a mat side and can perform activity processing of corona discharge treatment, flame treatment, etc. also to front flesh-side both sides a front face or if needed. Moreover, as thickness of a resin enveloping layer, although there is especially no limit, generally coating of it is carried out to the thickness of 5-50 micrometers of one side to a front face or front flesh-side both sides. The crack of an image with the passage of time improves by setting preferably to 0.1-4 micrometers 0.1-5 micrometers of with a cut OTOFU value [ of 0.8mm ] specified by JIS-B0601 of a field which prepares the ink absorbing layer of resin coat paper arithmetical mean deviation of profile by carrying out post processing of pressing a resin layer front face especially on the cooling roll by which mold attachment was carried out at the time of a resin coat, or the resin coat paper with a mold attachment roll etc. Since the solvent of the ink which sank in since the area of the interface which an ink absorbing layer and a resin enveloping layer touch by considering as the arithmetical mean deviation of profile of the above-mentioned range rather than the case where a resin enveloping layer front face is a mirror plane became large breadth-comes to be hard to the whole interface, it is guessed for lowering on the strength to decrease. If arithmetical mean deviation of profile is larger than 5 micrometers, the appearance of a feel or a printing image will fall.

[0027] Various kinds of back coat layers can be painted on the base material in this invention for antistatic nature, conveyance nature, curl tightness, etc. A back coat layer can be made to contain combining suitably an inorganic antistatic agent, an organic antistatic agent, a hydrophilic binder, a latex, a curing agent, a pigment, a surfactant, etc. Moreover, in order to raise the adhesive property of a base material and an ink absorbing layer, and compatibility, the under coat which contained the pigment, the hydrophilic binder, the latex, the curing agent, etc. suitably in the base material may be prepared.

[0028] Although the first [ an average of ] particle size is 1 micrometer or less and various well-known particles, such as a silica, an alumina, hydrated alumina, a calcium carbonate, and a magnesium carbonate, are mentioned as a non-subtlety particle used for the ink absorbing layer of this invention, especially a silica and hydrated alumina are desirable. In an ink absorbing layer, it is desirable to contain a non-subtlety particle two or more 8 g/m, and it is more desirable to it to use in the range of 10 - 40 g/m<sup>2</sup>. Ink absorptivity is inferior when fewer than this range. The amount of polyvinyl alcohol is below 35 mass % preferably below 40 mass % to a non-subtlety particle, and its 8 - 25 mass % is especially desirable.

[0029] As for the non-subtlety particle used in this invention, it is desirable to the main rate in an ink absorption layer, i.e., total solids, to contain a non-subtlety particle more

than 65 mass % more preferably more than 60 mass % more than 50 mass %.

[0030] There are what is depended on a wet method, and a thing to depend on a gaseous-phase method in a synthetic silica. The silica sol obtained as a wet method silica through the double decomposition and the ion-exchange-resin layer by an acid etc. of \*\* sodium silicate, or \*\* -- the colloidal silica obtained by carrying out heating aging of this silica sol -- \*\* The silica gel used as the three-dimensions-aggregated particle to which the several microns to about 10 microns primary particle carried out siloxane association by making a silica sol gel and changing the generation condition, Furthermore, although heating generation of \*\* silica sol, a sodium silicate, the sodium aluminate, etc. is carried out and it is obtained, there is a synthetic silicic-acid compound which makes a silicic acid [ like ] a subject.

[0031] A gaseous-phase method silica is also called dry process to a wet method, and, generally is made by flame hydrolysis. Although the approach of burning and specifically making tetrachlorosilane with hydrogen and oxygen is generally learned, silanes, such as methyltrichlorosilane and trichlorosilane, can be used in independent or the condition of having mixed with tetrachlorosilane, instead of tetrachlorosilane. From Japanese Aerosil, Inc., the gaseous-phase method silica is marketed as a QS type from Aerosil and Tokuyama, Inc., and can come to hand.

[0032] The mean particle diameter of the primary particle of the gaseous-phase method silica especially used for this invention preferably has desirable 5-30nm, and in order to acquire higher gloss, its 15nm or less is desirable. Furthermore, the mean particle diameter of a primary particle is 5-15nm preferably, and the specific surface area by the BET adsorption method is using the thing more than 200m<sup>2</sup>/g. The BET adsorption method as used in the field of this invention is one of the surface area measuring methods of the fine particles by the gas-phase-adsorption method, and is an approach of asking for the total surface area which a 1g sample has from adsorption isotherm, i.e., specific surface area. Usually, as an adsorption gas, many nitrogen gas is used and most approaches of measuring the amount of adsorption from \*\* of an adsorbed gas or change of the volume are used. The thing most prominent although the constant-temperature line of child adsorption is probably expressed is the formula of Brunauer, Emmett, and Teller, is called a BET equation and is widely used for surface area decision. The amount of adsorption is calculated based on a BET equation, the area which one admolecule occupies on a front face is applied, and surface area is obtained.

[0033] The gamma-alumina which is gamma mold crystal of an aluminum oxide as an alumina of this invention is desirable, and delta group crystal is desirable especially. Although gamma-alumina can make a primary particle small to about 10nm, what ground the thousands to tens of thousands of nm aggregated particle crystal to the very fine particle with the supersonic wave, a high voltage homogenizer, an opposite collision mold jet pulverizer, etc. can usually use it preferably.

[0034] The hydrated alumina preferably used by this invention is expressed with the constructive mood of aluminum<sub>2</sub>O<sub>3</sub> and nH<sub>2</sub>O (n=1-3). The case where n is 1 expresses the hydrated alumina of boehmite structure, and the case of less than three expresses [ n ] the hydrated alumina of pseudo-boehmite structure more greatly than 1. It is obtained by the well-known manufacture approaches, such as neutralization by hydrolysis of aluminum alkoxides, such as aluminum isopropoxide, and the alkali of an aluminum salt, and hydrolysis of an aluminate.

[0035] The mean particle diameter of the primary particle of the hydrated alumina used for this invention has desirable 5-50nm, and in order to acquire higher gloss, it is desirable that an average aspect ratio (ratio of mean particle diameter to average thickness) uses two or more plate-like particles by 5-30nm.

[0036] As for the ink absorbing layer of this invention, it is desirable to carry out to more than two-layer purpose-oriented, and the lower layer ink absorbing layer near a base material mainly aims at improvement in white nature and ink absorptivity the ink absorbing layer of the maximum upper layer which is separated from a base material for the purpose of improvement in glossiness, damage resistance, and weatherability. Since white nature is made high at a lower layer ink absorbing layer because the first [ an average of ] particle size uses preferably 5-50nm of 5-30nm non-subtlety particles and fluorescent brighteners, and the absorptivity of an ink solvent is raised especially, it is desirable. As for the ink absorbing layer of the upper layer which is separated from a base material, it is desirable from glossiness and weatherability that the first [ an average of ] particle size makes 5-30nm at least one sort of a hydrazine derivative, a \*\* sulfur organic compound, and a saccharide contain using a 5-20nm non-subtlety particle preferably. By making a lower layer ink absorbing layer contain the fluorescent brightener which affects yellowing etc., since minute gas or light in air cannot arrive easily to a lower layer, it is surmised that yellowing is eased more.

[0037] It is desirable from the xanthochroism of the blank paper section with the passage of time, the weatherability of the image section, and color enhancement to make a lower layer ink absorbing layer contain a non-subtlety particle and a fluorescent brightener, and to make the upper ink absorbing layer contain a non-subtlety particle and a cationic compound in this invention. The coloring material of ink is easy to be caught in the upper layer by making the upper ink absorbing layer contain a cationic compound, and it is guessed because lower layer fluorescent brightener and coloring material stop being able to contact easily. Moreover, since the xanthochroism of the blank paper section with the passage of time, the weatherability of the image section, and color enhancement improve in addition to the glossiness of the blank paper section improving by making a lower layer contain a non-subtlety particle and a fluorescent brightener, and using an alumina or hydrated alumina as a non-subtlety particle of the upper ink absorbing layer, it is desirable. That the above-mentioned effectiveness is acquired Although the coloring material of ink becomes is easy to be caught in the upper ink absorbing layer by making the upper ink absorbing layer contain a cationic compound, or using an alumina or hydrated alumina In addition, in addition to being hard coming to carry out contact of a lower layer fluorescent brightener and a coloring material, since a coloring material stops being able to permeate a lower layer ink absorbing layer easily, since minute gas or light in air cannot arrive easily to a lower layer, it is guessed because it is hard coming to yellow a lower layer fluorescent brightener. Since the weatherability and the crack with the passage of time of an image are improved because an aspect ratio uses two or more hydrated alumina for the ink absorbing layer of the maximum upper layer at least preferably, and ink absorptivity is also improved by using for a lower layer ink absorbing layer especially a gaseous-phase method [ the first / an average of / particle size is 5-30nm ] silica, it is desirable. Since the ink absorbing layer has a laminated structure of plate-like hydrated alumina, and a crack cannot occur easily in the shape of a straight line as compared with a spherical particle, and it is easy to concentrate a hydrophilic binder

on the interface between the plate-like particles of hydrated alumina, the reason the crack of an image with the passage of time is improved by plate-like hydrated alumina activity is guessed because bond strength becomes high.

[0038] As for a lower layer ink absorbing layer in case an ink absorbing layer is more than two-layer in this invention, it is desirable to make the amount of total solids into 5 - 30 g/m<sup>2</sup>, and its range of 10 - 25 g/m<sup>2</sup> is desirable especially from the improvement effectiveness in a whiteness degree, and ink absorptivity. The amount of solid content of the ink absorbing layer of the maximum upper layer has the desirable range of 1 - 15 g/m<sup>2</sup>, and its range of 1 - 12 g/m<sup>2</sup> is desirable especially from ink absorptivity.

[0039] the mean particle diameter of the non-subtlety particle of this invention asked for the diameter of circle equal to the projected area of each particle of 100 pieces which exists in fixed area by electron microscope observation of the distributed particle as a particle size of a particle. In a plate-like case, the mean particle diameter of the primary particle of the hydrated alumina of this invention is measured in the state of a flat surface. The average thickness of plate-like hydrated alumina is obtained from observation of the cutting side of the sheet which applied hydrated alumina on the film, and the aspect ratio of hydrated alumina is obtained by the ratio of mean particle diameter to average thickness.

[0040] Mean particle diameter may make the ink absorbing layer of this invention contain especially at least one sort of the spherical particle which is 3-20 micrometers 1 micrometers or more for amelioration of damage resistance, conveyance nature, and blocking nature. The former of the latter is [ the inorganic particle ] more more desirable from a feeling of a feel by the organic particle. Make a larger spherical particle than the thickness of the ink absorbing layer made to contain contain, it is [ direction ] desirable, carry out an ink absorbing layer to more than two-layer, and make it more desirable from damage resistance and glossiness for the maximum upper layer to contain a spherical particle. It is more desirable from tactile feeling not to project from an ink absorbing layer more greatly than 10 micrometers, although it is desirable that it is larger than the thickness of the ink absorbing layer of the maximum upper layer as for the mean particle diameter of a spherical particle.

[0041] By this invention, on an ink absorbing layer, by extent and solid content to which ink absorptivity is not reduced, it is 5g [ /m ] about [ 2 or less ], and the protective layer which made colloidal silica the subject may be prepared in order to improve damage resistance. Colloidal silica carries out heating aging of the silica sol obtained through the double decomposition and the ion-exchange-resin layer by an acid etc. of a sodium silicate, and is obtained. It is more desirable from ink absorptivity to form the aggregated particle whose mean particle diameter the mean particle diameter of the general primary particle of colloidal silica is about 5-100nm, and is about 10-500nm. as a commercial spherical thing -- the Nissan chemistry company make, Snow tex 20 grade, and a catalyst -- formation -- industrial company make, KATAROIDO USB, etc. are mentioned, the Nissan chemistry company make, the Snow tex UP, etc. are mentioned as a chain-like thing, and the Nissan chemistry company make, Snow tex PS-M, etc. can be used as a pearl necklace-like thing. A protective layer may also be made to contain at least one sort of the hydrazine derivative of this invention, a \*\* sulfur organic compound, and a saccharide. Moreover, it may add only to the spreading constituent of a protective layer without adding the hydrazine derivative of this invention, a \*\* sulfur organic compound,

or a saccharide to the spreading constituent of an ink absorbing layer, and an ink absorbing layer may be made to permeate.

[0042] In this invention, these derivatives, such as polyvinyl alcohol, starch, a carboxymethyl cellulose, hydroxyethyl cellulose, polyethylene oxide, polyacrylamide, and a polyvinyl pyrrolidone, are mentioned as a hydrophilic binder used with a non-subtlety particle in an ink absorbing layer. It is the polyvinyl alcohol or cation denaturation polyvinyl alcohol of perfect or partial saponification that polyvinyl alcohol is desirable, and it is important for transparency to be high, and for the higher permeability of ink to be acquired, to swell at the time of the osmosis in early stages of ink, and not to take up an opening although various denaturation objects, such as silanol denaturation and cation denaturation, are also contained, and it is especially desirable from this viewpoint.

[0043] one especially desirable also in polyvinyl alcohol -- whenever [ saponification ] -- 80% or more of part -- or full saponification is carried out. The thing of average degree of polymerization 200-5000 is desirable. As a hydrophilic binder used for the ink absorbing layer near especially a base material with a fluorescent brightener, it is desirable to use the polyvinyl alcohol of 80 - 93% of saponification degrees and average degree of polymerization 3000-5000 more than 50 mass % of a hydrophilic binder.

[0044] Moreover, it is polyvinyl alcohol which has the 1-3rd class amino group which is indicated by JP,61-10483,A, for example, and the 4th class ammonium in the principal chain of polyvinyl alcohol, or a side chain as cation denaturation polyvinyl alcohol.

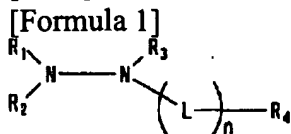
[0045] In this invention, xanthochroism-proof, the lightfastness of an image, and gas-proof nature improve by making an ink absorbing layer contain at least one sort of a hydrazine derivative, a \*\* sulfur organic compound, and a saccharide with a non-subtlety particle, a hydrophilic binder, and a fluorescent brightener. although the reason is unknown, the weatherability of the white nature which is each features by using a hydrazine derivative, a \*\* sulfur organic compound, and at least one sort and fluorescent brightener of a saccharide, and an image, and gas-proof nature improve in multiplication -- in addition, degradation which is the fault of a fluorescent brightener -- it is guessed because the stabilization effect of the coloring material which yellowing is suppressed and suppresses color-enhancing inhibition is acquired. When preparing an under coat, an ink absorbing layer, and a protective layer on a waterproof base material, at least one sort of a hydrazine derivative, a \*\* sulfur organic compound, and a saccharide is made to contain at least one sort of a hydrazine derivative, a \*\* sulfur organic compound, and a saccharide in an under coat, an ink absorbing layer or the ink absorbing layer of a protective layer that is preferably distant from a base material although you could make it contain at least any they were, and a protective layer, and an under coat or the ink absorbing layer near a base material is made to contain a fluorescent brightener. Since the direction which separates the layer which contains a fluorescent brightener especially, a hydrazine derivative, a \*\* sulfur organic compound, and the layer containing at least one sort of a saccharide improves further, xanthochroism-proof, the weatherability of an image, and its color enhancement are desirable. Here, an under coat is a layer in which a polymer compound subject and mean particle diameter contains comparatively big inorganic pigment and organic pigment, and a polymer compound 1 micrometers or more.

[0046] As a hydrazine derivative preferably used by this invention, there is a compound

of a publication in JP,61-154989,A, an application for patent No. 128984 [ 2001 to ], 2001-245125, etc., for example. A desirable thing is a thing of the structure expressed with the following-ization 1 inside.

[0047]

[Formula 1]



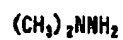
[0048] R1-R3 express a hydrogen atom, an aliphatic series radical, an aromatic series radical, and a heterocycle radical among the formula of \*\* 1. Moreover, R1 and R2 may be connected mutually and they may have cyclic structure. Inside, a desirable thing is an aliphatic series radical about R1 and R2, and its with a carbon number of four or less alkyl group is desirable especially. About R3, a hydrogen atom and an aliphatic series radical are desirable. R4 expresses a hydrogen atom, an aliphatic series radical, an aromatic series radical, a heterocycle radical, the amino group, and a hydrazino radical. Inside, desirable things are an aliphatic series radical, an amino group, and a hydrazino radical, and a with a carbon number of four or less alkyl group and the amino group, and its hydrazino radical are desirable especially. In addition, although R1-R4 of a more than may be permuted by the well-known substituent in this industry, about the amino group of R4, what is permuted by any one of a with a carbon number of six or less alkyl group, an alkoxy group, or the hydroxy groups is desirable. Similarly about a hydrazino radical, what is permuted by the thing by which the end nitrogen atom is permuted by two with a carbon number of four or less alkyl groups or a carbonyl group, an oxalyl radical, the sulfonyl group, the sulfoxy radical, the phosphoryl group, or the imino methylene group is desirable. And while stating above, especially a desirable thing is a methyl group about R1 and R2, and is the hydrazino radical permuted about R3 by the hydrogen atom and the amino group permuted about R4 by any one of a with a carbon number of six or less alkyl group, a methoxy group, and the hydroxy groups, the hydrazino radical by which the end nitrogen atom was permuted by two with a carbon number of four or less alkyl groups, or the carbonyl group.

[0049] L expresses a carbonyl group, an oxalyl radical, a sulfonyl group, the sulfoxy radical, a phosphoryl group, and an imino methylene group. Inside, desirable things are a carbonyl group and an oxalyl radical, and its carbonyl group is more desirable. The semicarbazide derivative whose R4 is the carbonohydrazide derivative whose R4 especially L is the hydrazino radical which is not permuted [ a permutation or ] in a carbonyl group and whose L is the amino group which is not permuted [ a permutation or ] in a carbonyl group is desirable. Although the example of the hydrazine derivative used for below by this invention is shown, this invention is not limited to these.

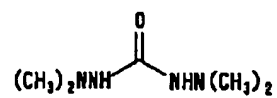
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[Formula 2]

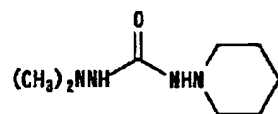
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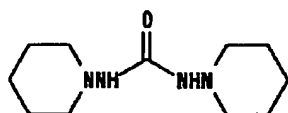
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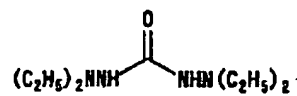
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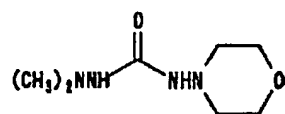
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H5



H6

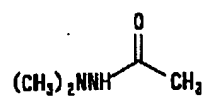


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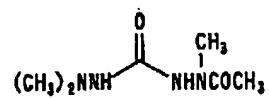
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H7



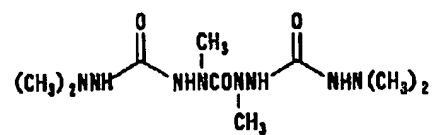
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H9



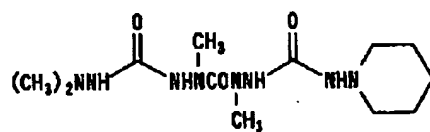
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H11



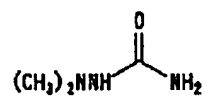
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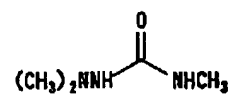
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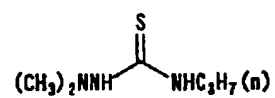
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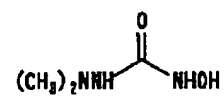
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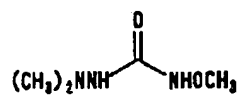
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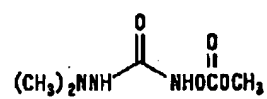
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H17



H18



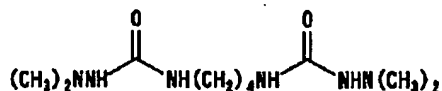
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[Formula 5]

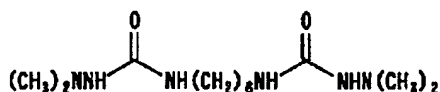
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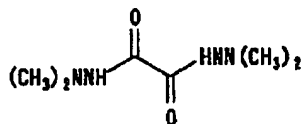
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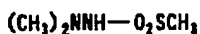
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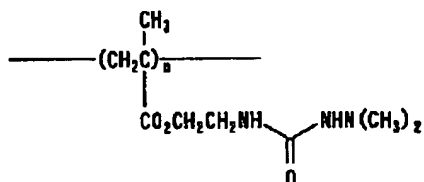
H22



H23



H24



[0054] It may add to a suitable solvent, or with an organic solvent, in polyvinyl alcohol, emulsification distribution may be carried out and the hydrazine derivative of this invention may add.

[0055] the total addition per unit area in the case of adding the hydrazine derivative of this invention to an ink absorbing layer -- 0.01 - 10 g/m<sup>2</sup> -- it is 0.05 - 3 g/m<sup>2</sup> preferably. If fewer than the above-mentioned range, it will be hard to come out of the endurance amelioration effectiveness of an image, and if many [ too ], ink absorptivity will fall, or it becomes easy to generate the crack of an image with the passage of time.

[0056] By this invention, a thioether compound, a thiourea system compound, a disulfide system compound, a mercapto compound, etc. are mentioned as a \*\* sulfur organic compound used.

[0057] There are an aromatic series system thioether compound which the aromatic series radical combined at the both sides of a sulfur atom, an aliphatic series system thioether

compound which has an alkyl group to the ends which sandwiched the sulfur atom at the thioether system compound of this invention. The aliphatic series thioether compound which has especially a hydrophilic radical is desirable. For example, 3, 6-dithio -1, 8-octanediol, a screw [2-(2-hydroxyethyl thio) ethyl] sulfone, 3 and 6, 9-TORICHIO -1, 11-undecane diol, 4-(methylthio) phenol, and 2-(phenylthio) ethanol are mentioned. As a thiourea system compound, specifically Thiourea, N-methyl thiourea, N-acetyl thiourea, 1, 3-diphenyl thiourea, tetramethyl thiourea, Guanylthiourea, 4-methylthio semicarbazide, 1, 3-screw (hydroxymethyl)-2 (3H) benzimidazole thione, The 6-hydroxy-1-phenyl -3, 4-dihydropyrimidine-2(1H)-thione, 1-allyl compound-2-thiourea, 1, 3-dimethyl-2-thiourea, 1, 3-diethyl-2-thiourea, ethylene thiourea, trimethyl thiourea, 1-carboxymethyl-2-thiohydantoin, thiosemicarbazide, etc. are mentioned. a disulfide system compound -- for example, - JICHIOJI morpholine, and DL-alpha-lipoic-acid, 4, and 4 '4, 4'-dithio -- a jib -- a tongue acid is desirable. A thiosalicylic acid system etc. and the nitrogen-containing heterocyclic compound of a mercapto compound are desirable, for example, 2-mercapto pyridine, a 3-hydroxy-2-mercapto pyridine, 2-mercaptobenzimidazole, 2-mercaptoimidazole, 2-mercaptopyrimidine, those derivatives, etc. are mentioned.

[0058] As a saccharide used by this invention, monosaccharides, such as D-glucose, D-ribose, a maltose, a cellobiose, a melibiose, a gentiobiose, D-glucosamine, D-xylose, D-galactose, a lactose, the vicianose, the turanose, gentianose, a rutinose, L-xylose, L-sorbose, D-mannitol, trehalose, D-fructose, a sucrose, a raffinose, and a stachyose, and oligosaccharide are mentioned, for example. Oligosaccharide is also called an oligosaccharide and says the sugar of the polymerization degree from a disaccharide to 15 sugar. The reducing sugar which have reduction radicals, such as D-glucose, a lactose, D-ribose, a maltose, and trehalose, more preferably are chosen from the effectiveness of lightfastness and gas-proof nature amelioration.

[0059] As a fluorescent brightener used for this invention, there are a pyrene derivative, a coumarin derivative, an oxazole derivative, a thiazole derivative, an imidazole derivative, an imidazolone derivative, a pyrazoline derivative, a benzidine derivative, etc. For example, a screw (triazinylamino) stilbene-disulfonic-acid salt derivative is marketed in Whitex series from Uvitex series and Sumitomo Chemical Co., Ltd., and is marketed [ Nippon Soda / Co., Ltd. / Chemicals / kayacoll series and / Tiba Speciality ] by trade names, such as Blankophor series, from Bayer. From the spreading nature and white nature of an ink absorbing layer, it is a water-soluble fluorescent brightener preferably, and a cationic fluorescent brightener is used especially preferably, for example, it is Uvitex in Tiba Speciality Chemicals. BAC is marketed.

[0060] while the solid content content of the fluorescent brightener contained in all ink absorbing layers has good white nature in this invention per unit area of an ink absorbing layer by 0.01 - 2 g/m<sup>2</sup> and considering as 0.05 - 1 g/m<sup>2</sup> preferably -- -proof -- the record ingredient for ink jets without the problem of yellowing, the color enhancement of an image, and weatherability is obtained. making a lower layer ink absorbing layer contain especially a fluorescent brightener, and not making the upper ink absorbing layer contain -- -proof -- from yellowing, the color enhancement of an image, and weatherability, it is desirable. By making a lower layer ink absorbing layer contain the fluorescent brightener which affects yellowing etc., since minute gas or light in air cannot arrive easily to a lower layer, it is surmised that yellowing is eased more.

[0061] After adding a fluorescent brightener in a hydrophilic binder solution and mixing in it as an approach of not making especially the upper ink absorbing layer containing a fluorescent brightener, but making the coating liquid of a lower layer ink absorbing layer containing a fluorescent brightener, the xanthochroism-proof of the obtained record ingredient and the color enhancement of an image become still better by mixing with non-subtlety particle dispersion liquid. Especially as a hydrophilic binder, it is desirable to use the polyvinyl alcohol of 80 - 95% of saponification degrees and average degree of polymerization 3000-5000 more than 50 mass % of a hydrophilic binder. It is guessed because migration to the upper ink absorbing layer is suppressed further in addition to protection of the fluorescent brightener which affects the weatherability of yellowing or an image and color enhancement.

[0062] It is desirable to use a cross linking agent (hardening agent) for an ink absorbing layer with a hydrophilic binder in this invention. As a concrete example of a cross linking agent, the aldehyde system compound like formaldehyde and glutaraldehyde, Diacetyl, the ketone compound like a KURORU 2,4-pentanedione, screw (2-chloro ethylurea)-2-hydroxy - 4, 6-dichloro-1,3,5-triazine, The compound which has a reactant halogen like a U.S. Pat. No. 3,288,775 publication, A divinyl sulfone, a compound with the reactant olefin like a U.S. Pat. No. 3,635,718 publication, N-methylol compound like a U.S. Pat. No. 2,732,316 publication, The isocyanate like a U.S. Pat. No. 3,103,437 publication, U.S. Pat. No. 3,017,280, The aziridine compounds like this No. 2,983,611 publication, and the carbodiimide system compounds like a U.S. Pat. No. 3,100,704 publication The epoxy compound like a U.S. Pat. No. 3,091,537 publication, and the halogen carboxy aldehydes like mucochloric acid the inorganic cross linking agent like the dioxane derivative like dihydroxy dioxane, chromium alum, a sulfuric-acid zirconium, and a \*\* boron compound etc. -- it is -- these -- one sort -- or two or more sorts can be combined and it can use. the inside of these -- especially -- a \*\* boron compound -- desirable -- a boric acid, a borate, a borax, etc. -- it is -- these -- one sort -- or two or more sorts can be combined and it can use. As a borate, an orthoboric acid salt, a metaboric acid salt, diborate, tetraborate, pentaborate, etc. are mentioned. the addition in the case of adding to an ink absorbing layer -- the solid content of a hydrophilic binder -- receiving -- 0.5 to 50 mass % -- it is one to 40 mass % preferably. If too few, it will be hard to acquire the amelioration effectiveness of the crack of an image with the passage of time, and if many [ too ], it will become easy to generate a crack in an ink absorbing layer at the time of the desiccation after carrying out coating.

[0063] In this invention, from the xanthochroism-proof of an image, it is desirable that the film surfaces pH measured from the upper ink absorbing layer front face are 3.5-6.0, and especially 3.5-5.5 are desirable. if pH is too high -- a file -- if yellowing is a lowering inclination and is too low -- degradation -- yellowing falls. The film surface pH of an ink absorbing layer is the front face pH measured after 30 seconds using distilled water according to the approach of a publication to the J.TAPPI paper pulp test method N0.49.

[0064] Although adjusting in the phase of coating liquid is desirable as for pH of an ink absorbing layer, in order that asking for the relation between coating liquid and a film surface pH by experiment etc. beforehand since it is not necessarily in agreement may make it the predetermined film surface pH, it is required for the film surface pH in the condition that spreading desiccation was carried out with pH of coating liquid. pH of coating liquid is performed combining an acid or alkali suitably. As an acid, organic

acids, such as inorganic acids, such as a hydrochloric acid, a nitric acid, a sulfuric acid, and a phosphoric acid, an acetic acid, a citric acid, and a succinic acid, are used, and the alkali-metal salt of weak acid, such as sodium acetate, is used as alkali as a sodium hydroxide, aqueous ammonia, potassium carbonate, phosphoric-acid 3 sodium, or weak alkali.

[0065] The more desirable mode of the ink absorbing layer of the hydrazine derivative in this invention, a \*\* sulfur organic compound, and the upper layer containing at least one sort of a saccharide \*\* The first [ an average of ] particle size of the non-subtlety particle which contains a cationic mordant, and contains and contains a fluorescent brightener is 30nm or less. Or front faces pH are 3.5-6.0, \*\* fluorescent brightener is not contained, but the alumina to contain or the first [ an average of ] particle size of hydrated alumina is 30nm or less, and front faces pH are 3.5-6.0. Glossiness is high and a record ingredient with the better color enhancement and weatherability of an image is obtained by the mode of above \*\* or \*\*. \*\* The upper ink absorbing layer may be made to contain a cationic mordant further in a mode.

[0066] Blank paper section xanthochroism and the color enhancement of an image improve by making the ink absorbing layer which constitutes the record ingredient for ink jets from this invention and which is preferably distant from a base material at least contain at least one layer of cationic compounds. As a cationic compound, water-soluble metallic compounds and a cationic polymer are used. As water-soluble metallic compounds, water-soluble polyvalent metallic salt is mentioned, for example. The water-soluble salt of the metal chosen from calcium, barium, manganese, copper, cobalt, nickel, aluminum, iron, zinc, a zirconium, chromium, magnesium, a tungsten, and molybdenum is mentioned. Specifically For example, calcium acetate, a calcium chloride, formic-acid calcium, A calcium sulfate, barium acetate, a barium sulfate, phosphoric-acid barium, a manganese chloride, Manganese acetate, a formic-acid man gunny hydrate, manganese-sulfate ammonium 6 hydrate, A cupric chloride, an ammonium-chloride copper (II) NI hydrate, a copper sulfate, a cobalt chloride, Thiocyanic acid cobalt, cobalt sulfate, nickel-sulfate 6 hydrate, nickel chloride 6 hydrate, Nickel acetate 4 hydrate, ammonium-nickel-sulfate 6 hydrate, amidosulfuric acid nickel 4 hydrate, An aluminum sulfate, sulfurous-acid aluminum, thiosulfuric-acid aluminum, a polyaluminum chloride, Aluminium nitrate 9 hydrate, the aluminum, the ferrous bromide, Ferrous chloride, a ferric chloride, a ferrous sulfate, ferric sulfate, a zinc bromide, a zinc chloride, Zinc nitrate 6 hydrate, a zinc sulfate, an acetic-acid zirconium, a zirconium nitrate, Zirconium chloride and chlorination zirconium dioxide 8 hydrate, a hydroxy zirconium chloride, Chromium acetate, chromium-sulfate, magnesium sulfate, and magnesium chloride 6 hydrate, Magnesium citrate 9 hydrate, \*\*\*\* sodium tungstate, a sodium-citrate tungsten, a 12 tongue strike phosphoric acid n hydrate, 12 tongue strike silicic-acid 26 hydrate, a molybdenum chloride, a 12 molybdo phosphoric acid n hydrate, etc. are mentioned.

[0067] In this invention, the water-soluble compound which contains a water-soluble aluminium compound or a periodic-table 4A group element especially is desirable. As mineral salt, as for the water-soluble aluminium compound, an aluminum chloride or its hydrate, an aluminum sulfate or its hydrate, an ammonium alum, etc. are known. Furthermore, there is a basic Pori aluminum-hydroxide compound which is the \*\* aluminum cation polymer of an inorganic system. Especially, the basic Pori aluminum-hydroxide compound is desirable.

[0068] said -- basicity -- Pori -- an aluminum hydroxide -- a compound -- a principal component -- the following -- a general formula -- one -- two -- or -- three -- being shown -- having -- for example, -- [-- aluminum -- six -- (-- OH --) -- 15 --] -- three -- + -- [-- aluminum -- eight -- (-- OH --) -- 20 --] -- four -- + -- [-- aluminum -- 13 -- (-- OH --) -- 34 --] -- five -- + -- [-- aluminum -- 21 -- (-- OH --) -- 60 --] -- three -- + -- etc. etc. -- like -- basicity -- a macromolecule -- polykaryotic -- condensation -- ion -- stability -- containing -- \*\*\*\* -- water solubility -- Pori -- an aluminum hydroxide -- it is .

[0069]

[aluminum<sub>2</sub>(OH)<sub>n</sub>Cl<sub>6-n</sub>]<sub>m</sub> General formula [ 3 ] 1 nAlCl [aluminum (OH)<sub>3</sub>] General formula 2Al<sub>n</sub>(OH)<sub>m</sub>Cl (3 n-m) 0< m<3n General formula 3 [0070] In the name of [ Chemistry / Asada ] the polyaluminum chloride (PAC), these things are the names of the Pori aluminum hydroxide (Paho), and are the names of PYURAKEMU WT from Riken Green, and Kamiichi is done by Taki Chemical Co., Ltd. with the same object as chemical for water treatment, from other manufacturers, and the object of various grade can obtain them easily from it. Although these commercial items can be used in this invention even if it remains as it is, it is also possible for an unsuitably low object to also have pH, and to adjust and use pH suitably in that case.

[0071] If there is a water-soluble compound containing the periodic table 4A group element used for this invention by water solubility, although there is especially no limit, its water-soluble compound containing titanium or a zirconium is desirable. For example, as a water-soluble compound containing titanium, an acetic-acid zirconium, a zirconium chloride, zirconium oxychloride, a hydroxy zirconium chloride, a zirconium nitrate, a basic carbonic acid zirconium, zirconium hydroxide, carbonic acid zirconium ammonium, the carbonic acid zirconium potassium, the sulfuric-acid zirconium, the fluoride zirconium compound, etc. are known as a water-soluble compound with which a titanium chloride and sulfuric-acid titanium contain a zirconium. As for these compounds, pH also has an unsuitably low object, and they are possible also for adjusting pH and using suitably in that case. Let it be a rule of thumb to dissolve in water 1% of the weight or more under ordinary temperature ordinary pressure with water solubility in this invention.

[0072] In this invention, 0.1 - 10 mass % of the content in the ink absorbing layer of the water-soluble above-mentioned metallic compounds is one to 5 mass % desirable still more preferably to a non-subtlety particle.

[0073] As a cationic polymer used in the ink absorbing layer of this invention Polyethyleneimine, a poly diaryl amine, the poly allylamine, an alkylamine polymerization object, JP,59-20696,A, 59-33176, 59-33177, 59-155088, 60-11389, 60-49990, 60-83882, 60-109894, 62-198493, 63-49478, 63-115780, 63-280681, The polymer which has the 1-3rd class amino group indicated by JP,1-40371,A, 6-234268, 7-125411, the 10-193776 official report, etc. and a quarternary-ammonium-salt radical is used preferably. As for the molecular weight of these cation polymers, 5,000 or more are desirable, and further 5,000 to about 100,000 are desirable.

[0074] the direction with little amount from the crack of an image of these cationic polymers used -- desirable -- a non-subtlety particle -- receiving -- one to 7 mass % -- it is two to 5 mass % preferably.

[0075] The record ingredient for ink jets is preferably constituted from this invention, and even if few, one layer of methylol amino system compounds is more preferably contained

in the ink absorbing layer of at least one layer. By this invention, a methylol amino system compound makes the monomer of a methylol amino system a configuration unit, and is a simple substance or a compound which carried out the polymerization, and the denatured methylol amino system compounds, such as an alkylation methylol amino system compound, are also contained. As a methylol amino system compound, a methylol melamine system compound, a methylolurea system compound, etc. are used. As an example, urea system compounds, such as melamine system compounds, such as the SUMIRE gap gin 613 by Sumitomo Chemical Co., Ltd., 8%AC, and 607syrup, SUMIRE gap gin 302, 636, 703, and 712, and EU, etc. are mentioned, and one or more sorts are used out of them. From the crack prevention effectiveness of the image of this invention with the passage of time, a methylol melamine system compound is used preferably. The addition in the case of adding to an ink absorbing layer is 0.5 to 50 mass % to the solid content of a hydrophilic binder, and is one to 30 mass % preferably. If too few, the crack amelioration effectiveness of an image will not be acquired, but if many [ too ], ink absorptivity will fall. Also when adding on each class of the record ingredient for ink jets, the same addition as an ink absorbing layer is desirable.

[0076] Although the reason the crack in the passage of time of a printing image is improved by this invention is unknown, it is guessed as follows about the case where each ingredient is added to an ink absorbing layer. By making an ink absorbing layer contain one or more sorts of a hydrazine derivative, a \*\* sulfur organic compound, and a saccharide, namely, the hydrogen bond of hydrophilic binders etc., Although association with a non-subtlety particle and a \*\*\*\* city-owned binder is checked, bonding strength becomes weak further with water and the organic solvent in ink by printing and it is easy to generate a crack It is the activity of a methylol amino system compound, and using together with a \*\* boron compound preferably. It is surmised that inhibition of association with the hydrophilic binders and non-subtlety particle by a hydrazine derivative etc., and a hydrophilic binder is suppressed by promoting association with the hydroxyl group of a hydrophilic binder etc. and the active group of a non-subtlety particle or those association. When water-soluble metallic compounds exist further in addition to a methylol amino system compound and a \*\* boron compound By those numbers of association increasing and strengthening bonding strength further, bonding strength does not decline with solvents, such as water in air and ink, but even if temperature and humidity change, it is surmised that it is hard that it comes to generate a crack in an image. pH of the coating liquid further that a methylol melamine system compound is desirable especially as a methylol amino system compound, and for ink absorbing layers - 3.5-6.0 -- carrying out -- an ink absorbing layer -- warming -- the reactivity of a methylol radical and the active group of a hydrophilic binder or a non-subtlety particle goes up by applying the temperature of 50 degrees C or more by processing etc., and it is surmised that the highly humid crack of the non-printed section of an ink absorbing layer and the crack of an image with the passage of time improve. Furthermore, probably because distortion becomes small by carrying out an ink absorbing layer to more than two-layer, the crack of an image with the passage of time improves rather than a monolayer.

[0077] In making the ink absorbing layer of this invention contain a methylol amino system compound For example, although coating and the approach of drying and forming an ink absorbing layer are common on a waterproof base material, a non-subtlety particle,



a fluorescent brightener, a \*\*\*\*\* compound, polyvinyl alcohol, a methylol amino system compound, and the coating liquid containing various additives for the ink absorbing layers of one or more layers. From activity degradation prevention of a methylol amino system compound or aging prevention of acidity or alkalinity. How to carry out coating of the coating liquid for ink absorbing layers and methylol amino system compound content liquid except a methylol amino system compound simultaneously. The coating liquid for ink absorbing layers except a methylol amino system compound. Coating, Methylol amino system compound content liquid is added just before coating in the main liquid for ink absorbing layers except the approach of carrying out coating of the methylol amino system compound content liquid, after drying, or a methylol amino system compound. The approach of carrying out coating after mixing is desirable, and since the crack of the approach of adding methylol amino system compound content liquid, and mixing with in-line one while sending the main liquid for ink absorbing layers especially of an image with the passage of time improves more, it is desirable. Since there is little activity degradation of a methylol amino system compound and homogeneity mixing is carried out into coating liquid as the reason, the number of association of a methylol amino system compound, and a polyvinyl alcohol and a non-subtlety particle increases, and it is guessed because it becomes strong. Just before coating is several seconds ago [ several minutes before carrying out coating generally ] here. As mixed equipment used after adding 2 liquid, the equipment with which the in-line mixer, the static mixer, etc. are marketed from Kenics, Sulger, Kohritz, and Toray Industries, Inc., for example can be used. Moreover, a highly humid crack and the crack in the passage of time of a printing image improve further by making preferably 50 degrees C or more of skin temperature of an ink absorbing layer into 60 degrees C or more at the desiccation process after the decreasing drying after carrying out coating of the coating liquid of methylol amino system compound content. warming to which the skin temperature of an ink absorbing layer becomes 50 degrees C or more with another line about a process until it rolls round a record ingredient original fabric, and the record ingredient original fabric after rolling round after the moisture of an ink absorbing layer makes it dry below to 10 mass % extent at a desiccation process -- a highly humid crack and the crack by the passage of time of a printing image are improved performing a process. warming -- the environmental temperature of a process -- warming -- although based on time amount, it is the temperature in which degradation of a record ingredient with the passage of time does not occur -- especially about 100 degrees C or less are desirable 150 degrees C or less. Although the time amount to warm changes with temperature, several hours are suitable from several seconds. Since generating of the wind ripple at the time of desiccation can be suppressed by cooling preferably about 20 degrees C or less of coating liquid for ink absorbing layers in which coating was carried out by the cooling process just before the desiccation process at 15 degrees C or less, it is desirable.

[0078] In this invention, various additives with still better known fixing agent of a surfactant, a coloring color, a color pigment, and an ink color, ultraviolet ray absorbent, anti-oxidant, deck-watertight-luminaire-ized agent, dispersant of a pigment, defoaming agent, leveling agent, antiseptics, viscosity stabilizer, etc. can also be added in an ink absorbing layer.

[0079] In the ink absorbing layer of this invention, in order to improve the brittleness of a

coat further, various oil droplets can be contained. The solubility over the water in a room temperature can make the hydrophobic high-boiling point organic solvents (for example, a liquid paraffin, dioctyl phthalate, tricresyl phosphate, a silicone oil, etc.) and polymer particle (for example, particle to which the polymerization of the polymerization nature monomers, such as styrene, butyl acrylate, a divinylbenzene, butyl methacrylate, and hydroxyethyl methacrylate, was carried out more than a kind) below 0.01 mass % contain as such an oil droplet. Such an oil droplet can be preferably used in the range of 10 - 50 mass % to a hydrophilic binder.

[0080] In this invention, especially the method of application in the case of preparing the method of application of an ink absorbing layer and an under coat, and a protective layer is not limited, but the well-known method of application can be used for it. For example, there are a slide bead method, a curtain method, an extrusion method, an air knife method, a roll coating method, a rod bar coating method, etc.

[0081]

[Example] Hereafter, although an example explains this invention in detail, the content of this invention is not restricted to an example. In addition, the section means the solid content mass section.

[0082] As example 1 base material 25g/[m ] 2 melting extrusion spreading of the resin constituent which becomes the front face of the base paper of 170 g/m<sup>2</sup> which consists of pulp combination of LBKP (50 sections) and LBSP (50 sections) from low density polyethylene (70 sections), high density polyethylene (20 sections), and titanium oxide (ten sections) is carried out. A right face resin enveloping layer The resin coat paper which prepared, carried out 25 g/m<sup>2</sup> melting extrusion spreading of the resin constituent which consists of high density polyethylene (50 sections) and low density polyethylene (50 sections), and prepared the rear-face resin enveloping layer in the rear face was prepared.

[0083] After performing high frequency corona discharge treatment to the right face resin enveloping layer of the above-mentioned resin coat paper, spreading desiccation of the under-coating layer of the following presentation was carried out so that gelatin might serve as 50 mg/m<sup>2</sup>, and the base material was created. In addition, the section expresses the mass section.

[0084]

<Under-coating layer> liming gelatin 100 section sulfo succinic-acid-2-ethylhexyl ester salt 2 section chromium alum The ten sections [0085] On the above-mentioned base material, the lower layer following spreading constituent 1 for ink absorbing layers and the upper spreading constituent 1 for ink absorbing layers were adjusted, it dried by spreading by the slide bead method, dried in order (40 degrees C and 60 degrees C) after cooling at 10 degrees C, and the record ingredient for ink jets of an example 1 was created so that the coverage of a gaseous-phase method silica might be set to 12g of lower layers/, m<sup>2</sup>, and 10g of upper layers/and m<sup>2</sup> by solid content. A potassium hydroxide solution adjusted so that the film surface pH measured from the upper ink absorbing layer might be set to 4.0. At the time of the lower layer spreading constituent 1 adjustment for ink absorbing layers, the fluorescent brightener was added to gaseous-phase method silica dispersion liquid, after adding and mixing in a polyvinyl alcohol water solution.

[0086]

<Lower layer spreading constituent 1 for ink absorbing layers> Gaseous-phase method silica The 100 sections (specific-surface-area 300m<sup>2</sup>/g by the first [ an average of ] particle size of 7nm, and the BET adsorption method)  
 Dimethyl diaryl ammoniumchloride homopolymer The four sections (the Dai-Ichi Kogyo Seiyaku Co., Ltd. make, Shallol DC902P, molecular weight 9000)  
 Polyvinyl alcohol The 26 sections (trade name-VA235, Kuraray Co., Ltd. Make, 88% of saponification degrees, average degree of polymerization 3500)  
 Fluorescent brightener The one section (trade name: UVITEX BAC, made in Tiba Speciality Chemicals)  
 Way acid The five sections Amphoteric surface active agent The 0.3 sections (trade name: SWAM AM-2150, Japanese surfactant company make)

[0087]

The <upper spreading constituent 1 for ink absorbing layers> Gaseous-phase method silica The 100 sections (specific-surface-area 300m<sup>2</sup>/g by the first [ an average of ] particle size of 7nm, and the BET adsorption method)  
 Dimethyl diaryl ammoniumchloride homopolymer The four sections (the Dai-Ichi Kogyo Seiyaku Co., Ltd. make, Shallol DC902P, molecular weight 9000)  
 Polyvinyl alcohol The 20 sections (trade name-VA235, Kuraray Make, 88% of saponification degrees, average degree of polymerization 3500)  
 Way acid The five sections Amphoteric surface active agent The 0.3 sections (trade name: SWAM AM-2150, product made from the Japanese surfactant)  
 Water-soluble metallic compounds: Basic Pori aluminum hydroxide The four sections (trade name: PYURAKEMU WT, made in Riken Green)

Compound of \*\* 2 (H1) The five sections Methylol melamine system compound The two sections (the Sumitomo Chemical Co., Ltd. make, SUMIRE gap gin 613)

[0088] The record ingredient for ink jets of an example 2 was obtained like the example 1 except having replaced with the compound (H1) of \*\* 2 of an ink absorbing layer presentation in the example 2 example 1, and having used the compound (H3) of \*\* 2.

[0089] The record ingredient for ink jets of an example 3 was obtained like the example 1 except having replaced with the compound (H1) of \*\* 2 of an ink absorbing layer presentation in the example 3 example 1, and having used the compound (H16) of \*\* 4.

[0090] The record ingredient for ink jets of an example 4 was obtained like the example 1 except having replaced with the compound (H1) of \*\* 2 of an ink absorbing layer presentation in the example 4 example 1, and having used the compound (H20) of \*\* 5.

[0091] The record ingredient for ink jets of an example 5 was obtained like the example 1 except having replaced with the compound (H1) of \*\* 2 of an ink absorbing layer presentation in the example 5 example 1, and having used the compound (H21) of \*\* 5.

[0092] The record ingredient for ink jets of an example 6 was obtained like the example 1 except having replaced with the compound (H1) of \*\* 2 of an ink absorbing layer presentation in the example 6 example 1, and having used 3, 6-dithio -1, and 8-octanediol.

[0093] The record ingredient for ink jets of an example 7 was obtained like the example 1 except having replaced with the compound (H1) of \*\* 2 of an ink absorbing layer presentation in the example 7 example 1, and having used the 3-hydroxy-2-mercapto pyridine.

[0094] The record ingredient for ink jets of an example 8 was obtained like the example 1

except having replaced with the compound (H1) of \*\* 2 of an ink absorbing layer presentation in the example 8 example 1, and having used D-glucose.

[0095] The record ingredient for ink jets of an example 9 was obtained like the example 1 except having replaced with the water-soluble metallic compounds of the upper spreading constituent for ink absorbing layers in the example 9 example 1, and having used the cationic polymer (the Satoda Kako, Ltd. make, jet fix 30).

[0096] The record ingredient for ink jets of an example 10 was obtained like the example 1 in the example 10 example 1 except having added the 4 sections (the Satoda Kako, Ltd. make, jet fix 30) of cationic polymers to the upper spreading constituent for ink absorbing layers further.

[0097] The record ingredient for example 11 ink jets was obtained like the example 1 in the example 11 example 1 except having extracted the water-soluble metallic compounds of an activity in the upper ink absorbing layer.

[0098] The record ingredient for ink jets of an example 12 was obtained like the example 1 except a potassium hydroxide solution having adjusted so that the film surface pH measured from the upper ink absorbing layer in the example 12 example 1 might be set to 5.8.

[0099] The record ingredient for ink jets of an example 13 was obtained like the example 1 except the nitric-acid solution having adjusted so that the film surface pH measured from the upper ink absorbing layer in the example 13 example 1 might be set to 3.1.

[0100] The record ingredient for ink jets of an example 14 was obtained like the example 1 in the example 14 example 1 except having extracted the upper methylol melamine system compound.

[0101] In the example 15 example 1, the spreading constituent 1 for ink absorbing layers of a lower layer and the upper layer was replaced with the spreading constituent 2 for ink absorbing layers of the following lower layer and the upper layer, it simultaneous-applied, dried and the record ingredient for ink jets of an example 15 was obtained so that it might become 9 g/m<sup>2</sup> by the solid about the hydrated alumina of 15 g/m<sup>2</sup> and the upper layer by the solid in a lower layer gaseous-phase method silica. A potassium hydroxide solution adjusted so that the film surface pH measured from the upper ink absorbing layer might be set to 4.0. At the time of the lower layer spreading constituent 2 adjustment for ink absorbing layers, the fluorescent brightener was added to gaseous-phase method silica dispersion liquid, after adding and mixing in a polyvinyl alcohol solution.

[0102]

<Lower layer spreading constituent 2 for ink absorbing layers> Gaseous-phase method silica The 100 sections (specific-surface-area 200m<sup>2</sup>/g by the first [ an average of ] particle size of 12nm, and the BET adsorption method)

Dimethyl diaryl ammoniumchloride homopolymer The four sections (the Dai-Ichi Kogyo Seiyaku Co., Ltd. make, Shallol DC902P, molecular weight 9000)

Way acid The three sections Polyvinyl alcohol The 15 sections (trade name-VA235, Kuraray Make, 88% of saponification degrees, average degree of polymerization 3500)

Fluorescent brightener The one section (trade name: UVITEX BAC, made in Tiba Speciality Chemicals)

Amphoteric surface active agent The 0.3 sections (trade name: SWAM AM-2150, Japanese surfactant company make)

[0103]

The <upper spreading constituent 2 for ink absorbing layers> Hydrated alumina The 100 sections (the first [ an average of ] particle size of 14nm, plate-like particle of an aspect ratio 5)

A nitric acid The one section Way acid The 0.5 sections Polyvinyl alcohol The 15 sections (trade name-VA235, Kuraray Make, 88% of saponification degrees, average degree of polymerization 3500)

Surfactant The 0.5 sections Compound of-izing 2 (H1) The five sections Methylol melamine system compound The two sections (the Sumitomo Chemical Co., Ltd. make, SUMIRE gap gin 613)

[0104] The record ingredient for ink jets of an example 16 was similarly obtained except having considered as the ink absorbing layer of a monolayer so that it might become 22 g/m<sup>2</sup> about the solid content coverage of a gaseous-phase method silica using the following spreading constituent 3 for ink absorbing layers in an ink absorbing layer in the example 16 example 1. In addition, at the time of the spreading constituent 3 adjustment for ink absorbing layers, the fluorescent brightener was added to gaseous-phase method silica dispersion liquid, after adding and mixing in a polyvinyl alcohol solution.

[0105]

<Spreading constituent 3 for ink absorbing layers> Gaseous-phase method silica The 100 sections (specific-surface-area 300m<sup>2</sup>/g by the first [ an average of ] particle size of 7nm, and the BET adsorption method)

Dimethyl diaryl ammoniumchloride homopolymer The four sections (the Dai-Ichi Kogyo Seiyaku Co., Ltd. make, Shallol DC902P, molecular weight 9000)

Polyvinyl alcohol The 20 sections (trade name-VA235, Kuraray Make, 88% of saponification degrees, average degree of polymerization 3500)

Fluorescent brightener The 0.4 sections (trade name: UVITEX BAC, made in Tiba Speciality Chemicals)

Way acid The five sections Amphoteric surface active agent The 0.3 sections (trade name: SWAM AM-2150, product made from the Japanese surfactant)

Water-soluble metallic compounds: Basic Pori aluminum hydroxide The four sections (trade name: PYURAKEMU WT, made in Riken Green)

Compound of \*\* 2 (H1) The 2.1 sections Methylol melamine system compound The two sections (the Sumitomo Chemical Co., Ltd. make, SUMIRE gap gin 613)

[0106] The record ingredient for example 17 ink jets was obtained like the example 16 except having replaced the fluorescent brightener of an activity with UVITEXBFA (made in Tiba Speciality Chemicals) from UVITEX BAC in the ink absorbing layer of a lower layer [ example 17 example 16 ].

[0107] The record ingredient for example 18 ink jets was obtained like the example 1 in the example 18 example 1 except having extracted the compound (H1) of \*\* 2 of an activity in the upper ink absorbing layer.

[0108] The record ingredient for example 19 ink jets was obtained like the example 15 in the example 19 example 15 except having extracted the compound (H1) of \*\* 2 of an activity in the upper ink absorbing layer.

[0109] The record ingredient for ink jets of the example 1 of a comparison was obtained from the ink absorbing layer like the example 16 in the example of comparison 1 example 16 except having extracted the fluorescent brightener and the methylol melamine system compound.

[0110] The record ingredient for ink jets of the example 2 of a comparison was obtained from the ink absorbing layer like the example 16 in the example of comparison 2 example 16 except having extracted the compound (H1) of \*\* 2, and the methylol melamine system compound.

[0111] The record ingredient for ink jets of the example 3 of a comparison was obtained from the ink absorbing layer like the example 16 in the example of comparison 3 example 16 except having extracted a fluorescent brightener, the compound (H1) of \*\* 2, water-soluble metallic compounds, and a methylol melamine system compound.

[0112] About each obtained record ingredient for ink jets, xanthochroism-proof [ white nature and ], ink absorptivity, the image shelf life after printing (lightfastness and gas-proof nature), and the color enhancement of an image were evaluated by 23 degrees C and 50%RH by the following after the passage of time one whole day and night. The result is shown in a table 1.

[0113] Viewing estimated the whiteness under a <white nature> fluorescent lamp on the following criteria.

O; it has very good whiteness.

O; it has good whiteness.

\*\*; it is the whiteness of the yellow taste a little.

x; it is a yellow taste and whiteness is insufficient.

[0114] Viewing compared whiteness under the fluorescent lamp and the following criteria estimated the sample irradiated by 600 W/m<sup>2</sup> for 30 hours with the SANTESUTO CPS photofading testing machine by the <xanthochroism-proof> atlas company, and the sample which was not irradiated.

O; almost with no change.

\*\*; it is change owner \*\* a little.

x; change is large.

[0115] Using the <ink absorptivity> ink jet printer (Seiko Epson PM-800C), C, M, and Y were printed at 100%, respectively, the PPC form was lightly stuck to the printing section by pressure in piles immediately after printing, extent of the amount of ink imprinted in the PPC form was observed visually, and the following criteria estimated.

O : don't imprint at all.

\*\* : A real activity is possible although imprinted a little.

x: Imprint and a real activity is impossible.

[0116] After the ink of CYMK having performed solid printing using the <light-fast> ink jet printer (Seiko Epson PM-800C), respectively and irradiating by 600 W/m<sup>2</sup> with the SANTESUTO CPS photofading testing machine by the atlas company for 50 hours, the concentration of the printing section was measured, the image survival rate (concentration before after [ an exposure ] concentration / exposure) was searched for, and what has the lowest survival rate was displayed among CMYK images.

[0117] Like the <gas-proof nature> above-mentioned radiationproofing test, after printing, after being exposed to the indoor wall surface for 100 days at the room temperature, the concentration of the printing section was measured, the image survival rate (concentration before after [ exposure ] concentration / exposure) was searched for, and what has the lowest survival rate was displayed among CMYK images.

[0118] The ink jet printer (Seiko Epson PM-800C) was used for <color-enhancing> each record ingredient, solid printing of C, G, Y, R, M, and B was performed, the data of a\*

specified by each JIS-Z8730 and b\* were entered in the a\*-b\* coordinate, and the area which connected in a straight line and was surrounded compared each point. Color enhancement was good, and the one where area is larger made the example 3 of a comparison O, and evaluated it by the following criteria.

O \*\* which has the same good color enhancement as the example 3 of; comparison; color enhancement falls a little from the example 3 of a comparison.

x; color enhancement falls greatly from the example 3 of a comparison.

[0119] The following criteria estimated the crack of a printing side for the sheet of the bottom which left in piles cyanogen, a Magenta, and five sheets that printed 300% of 3 color overlapping of yellow in 23 degrees C and the environment of 50%RH one whole day and night, and took them out with the <passage-of-time crack of image> ink jet printer (the Seiko Epson make, MC2000) after neglect one whole day and night.

O : completely with no crack.

\*\* : -- detailed to a part -- with [ in a real activity ] no problem although it crocodiles.

x: They are those with a crack to the whole surface.

[0120]

[A table 1]

-----	White nature	Xanthochroism-proof	Ink Shelf life (%)	Color enhancement	Image section	Absorptivity	Lightfastness	Gas-proof nature	A crack	-----	
-----	example 1	O O O	88 90	O O	Example 2	O O O	89 90	O O			
Example 3	O O O	90 92	O O	Example 4	OO O	88 91	O O	Example 5	O O O	87 91 O O	
Example 6	O **	O 85 90	O O	example 7	O **	O 85 88	** O	Example 8	O **	O 84 86 O	
O	Example 9	OO O	85 88	O O	Example 10	OO O	90 91	O O	Example 11	O O O	85 87 O
O	Example 12	O **	O 89 87	OO	Example 13	O **	O 85 91	O O	Example 14	OO O	87 90
O **	example 15	O OO	86 88	O O	Example 16	O**	O 84 86	** O	Example 17	****	O
85 87	**O	Example 18	OO O	80 73	OO	Example 19	O O O	81 74	O O	-----	
-----	Example 1 of comparison	x **	O 87 90	**x	Example 2 of a comparison	O x					
O75	Example 3 of 69	** **	comparison	x **O	76 71	O **	-----				

[0121] Glossiness had glossiness with any expensive record ingredient.

[0122] The record ingredient of examples 1-19 indicated that a good property was clear from the above-mentioned result. The record ingredient of the example 1 of a comparison which extracted the fluorescent brightener and the methylol melamine system compound from the ink absorbing layer of a lower layer [ an example 16 ] was inferior to the crack of white nature and an image with the passage of time. As for the example 2 of a comparison which extracted the hydrazine derivative of an ink absorbing layer, and the methylol melamine system compound in the example 16, xanthochroism-proof, and the lightfastness and gas-proof nature of an image fell greatly. Although the color enhancement of the example 3 of a comparison which extracted the Hilo Rajin derivative, water-soluble metallic compounds, and a methylol melamine system compound in the example 16 was good, the lightfastness and gas-proof nature of white nature and an image fell greatly.

[0123]

[Effect of the Invention] According to this invention, glossiness, white nature, and ink absorptivity are good, and the record ingredient for ink jets excellent in the weatherability of an image and color enhancement is obtained.